US009182352B2

(12) **United States Patent**
**Wang et al.**

(10) **Patent No.: US 9,182,352 B2**
(45) **Date of Patent: *Nov. 10, 2015**

(54) **SYSTEM AND METHOD FOR DETECTING OIL OR GAS UNDERGROUND USING LIGHT SCATTERING SPECTRAL ANALYSES**

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(73) Assignee: **OptoTrace (SuZhou) Technologies, Inc.**, Suzhou (CN)

( * ) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 41 days.

This patent is subject to a terminal disclaimer.

(21) Appl. No.: **14/051,396**

(22) Filed: **Oct. 10, 2013**

(65) **Prior Publication Data**

US 2014/0043607 A1 Feb. 13, 2014

**Related U.S. Application Data**

(63) Continuation of application No. 13/080,142, filed on Apr. 5, 2011, now Pat. No. 8,582,099, which is a continuation-in-part of application No. 12/502,903, filed on Jul. 14, 2009, now Pat. No. 7,929,133, which

(Continued)

(51) **Int. Cl.**

| | |
|---|---|
| ***G01J 3/44*** | (2006.01) |
| ***G01N 21/65*** | (2006.01) |
| ***B82Y 20/00*** | (2011.01) |
| ***G01N 33/543*** | (2006.01) |
| ***G01J 3/02*** | (2006.01) |
| *B82Y 40/00* | (2011.01) |

(52) **U.S. Cl.**

CPC ................ ***G01N 21/65*** (2013.01); ***B82Y 20/00*** (2013.01); ***G01J 3/0264*** (2013.01); ***G01J 3/44*** (2013.01); ***G01N 21/658*** (2013.01); ***G01N 33/54346*** (2013.01); *B82Y 40/00* (2013.01)

(58) **Field of Classification Search**

CPC ................ G01N 21/65; G01N 21/658; G01N 2021/656; G01J 3/02; G01J 3/44

USPC .............................................. 356/301, 72–73

See application file for complete search history.

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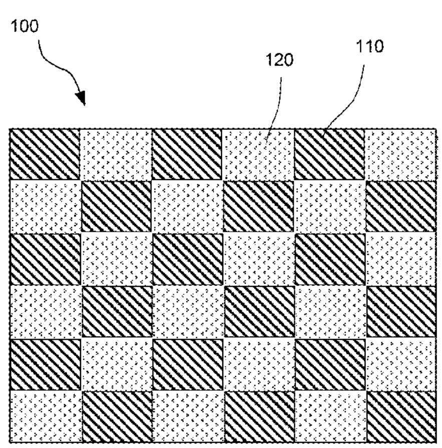
*Primary Examiner* — Abdullahi Nur
(74) *Attorney, Agent, or Firm* — SV Patent Service

(57) **ABSTRACT**

A method for detecting crude oil or gas in a drilling sample includes introducing a drilling sample into a sample solution containing nano particles, illuminating the sample solution comprising the drilling sample and the nano particles by a laser beam, collecting light scattered by the drilling sample and the nano particles in the sample solution, obtaining a Raman spectrum from the light scattered by the drilling sample and the nano particles in the sample solution, identifying, in the Raman spectrum, a spectral signature associated with a substance around a predetermined Raman shift, and detecting targeted chemicals correlated with crude oil or gas existence underground from where the drilling sample, based on the spectral signature of the substance in the Raman spectrum.

**25 Claims, 52 Drawing Sheets**



**Related U.S. Application Data**

is a continuation-in-part of application No. 12/262,667, filed on Oct. 31, 2008, now Pat. No. 7,576,854, which is a continuation-in-part of application No. 11/562,409, filed on Nov. 21, 2006, now Pat. No. 7,460,224, said application No. 13/080,142 is a continuation-in-part of application No. 12/625,970, filed on Nov. 25, 2009, now Pat. No. 8,213,007, which is a continuation-in-part of application No. 12/403,522, filed on Mar. 13, 2009, now Pat. No. 8,102,525, said application No. 13/080,142 is a continuation-in-part of application No. 12/643,689, filed on Dec. 21, 2009, now Pat. No. 8,081,308.

(60) Provisional application No. 60/751,472, filed on Dec. 19, 2005.

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* cited by examiner

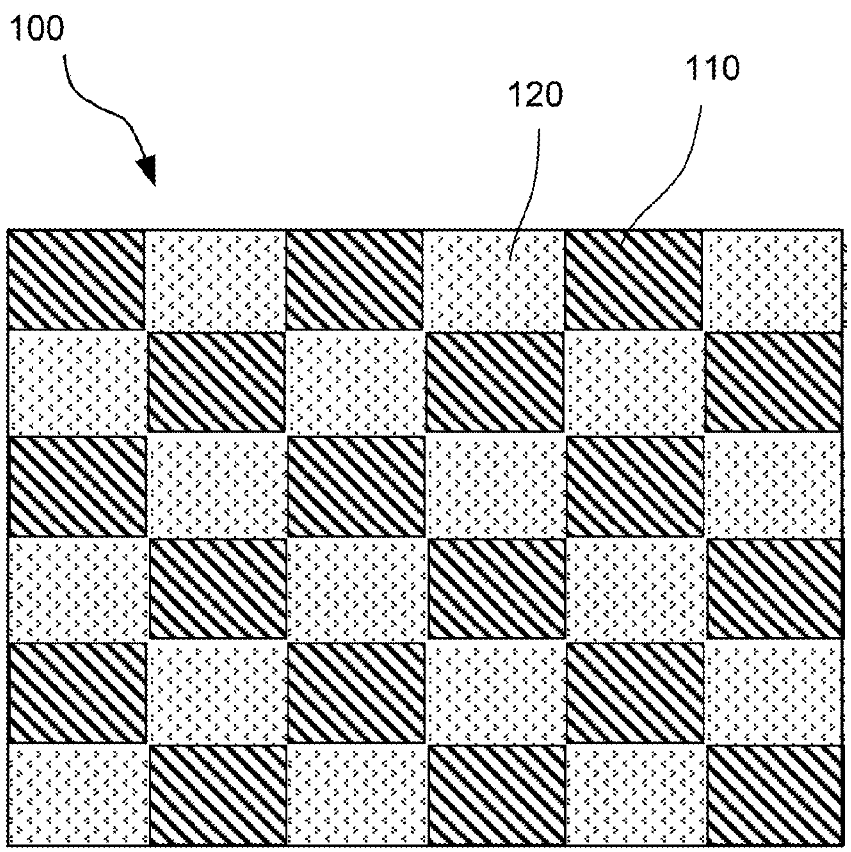



FIG. 1

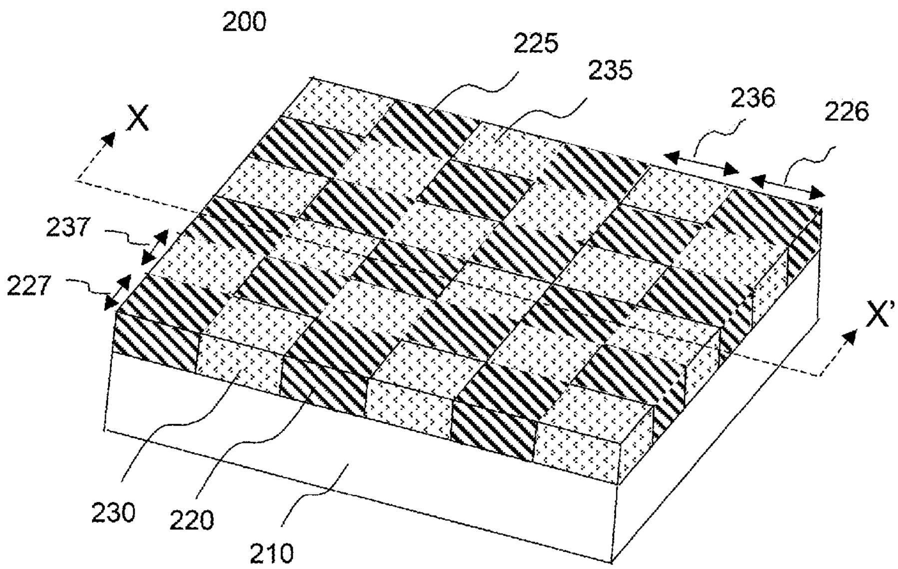
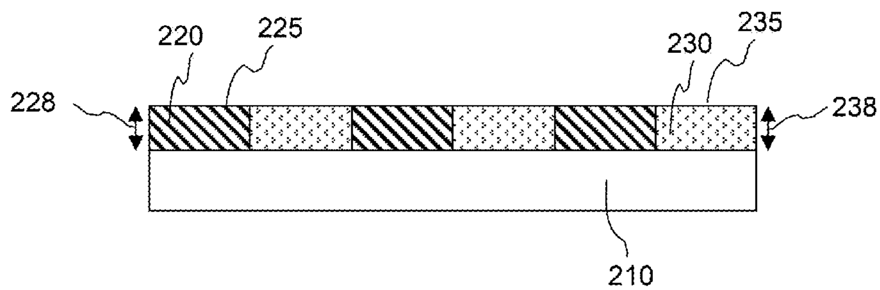

200
225
235
236
226
X
237
227
X'
230
220
210

FIG. 2A


220
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210

FIG. 2B

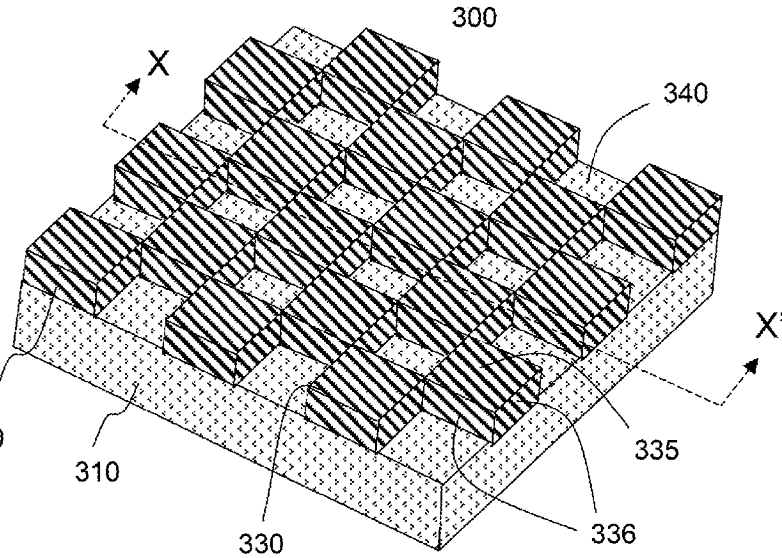



FIG. 3A

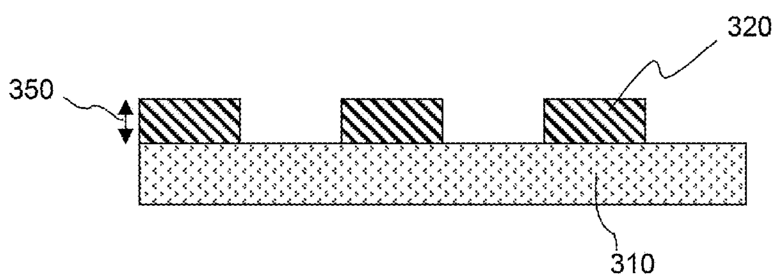



FIG. 3B

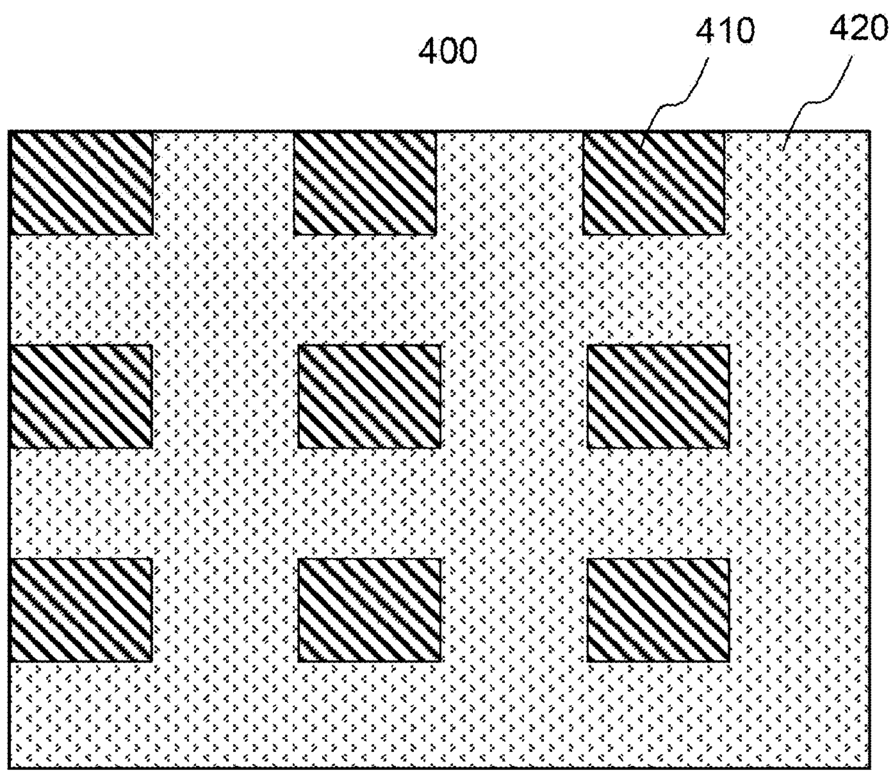



FIG. 4

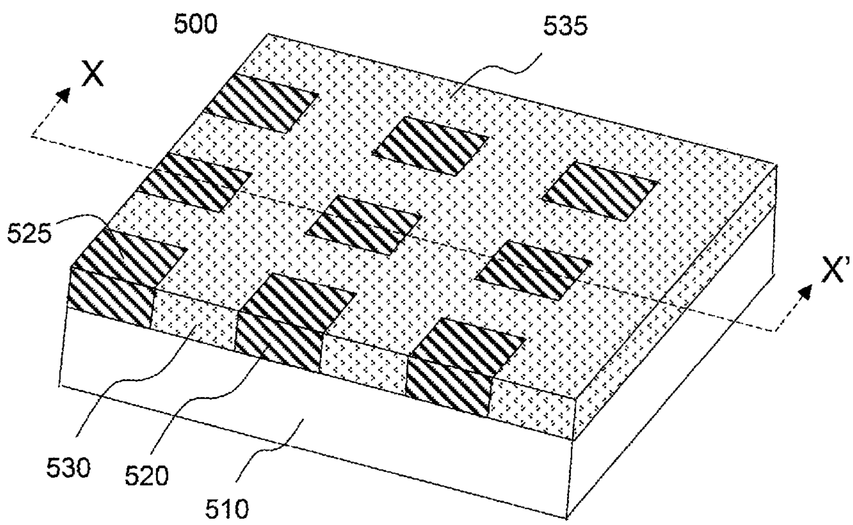



FIG. 5A

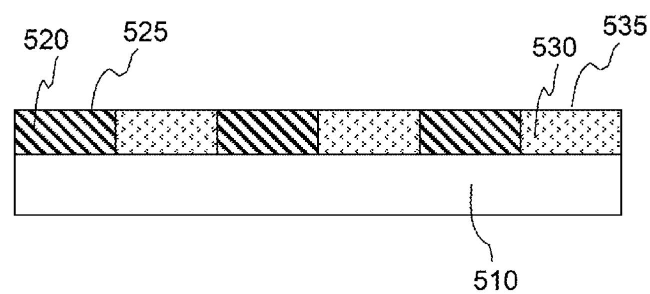



FIG. 5B

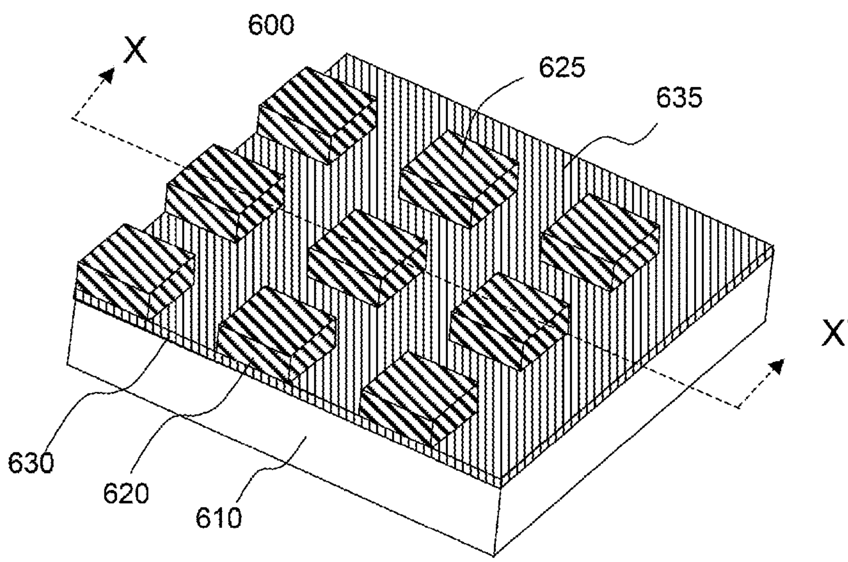



FIG. 6A

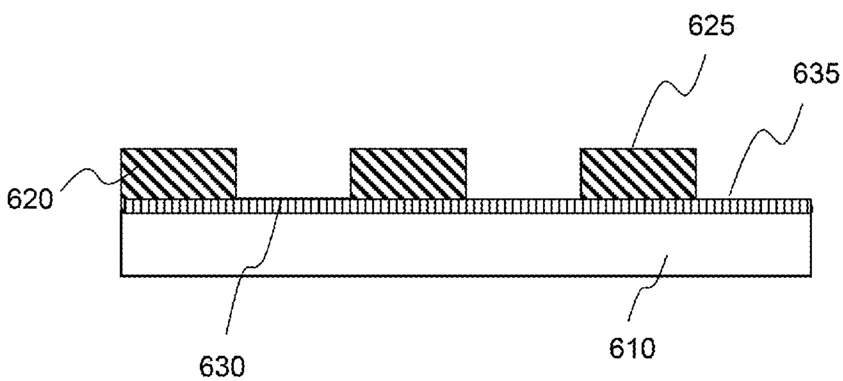



FIG. 6B

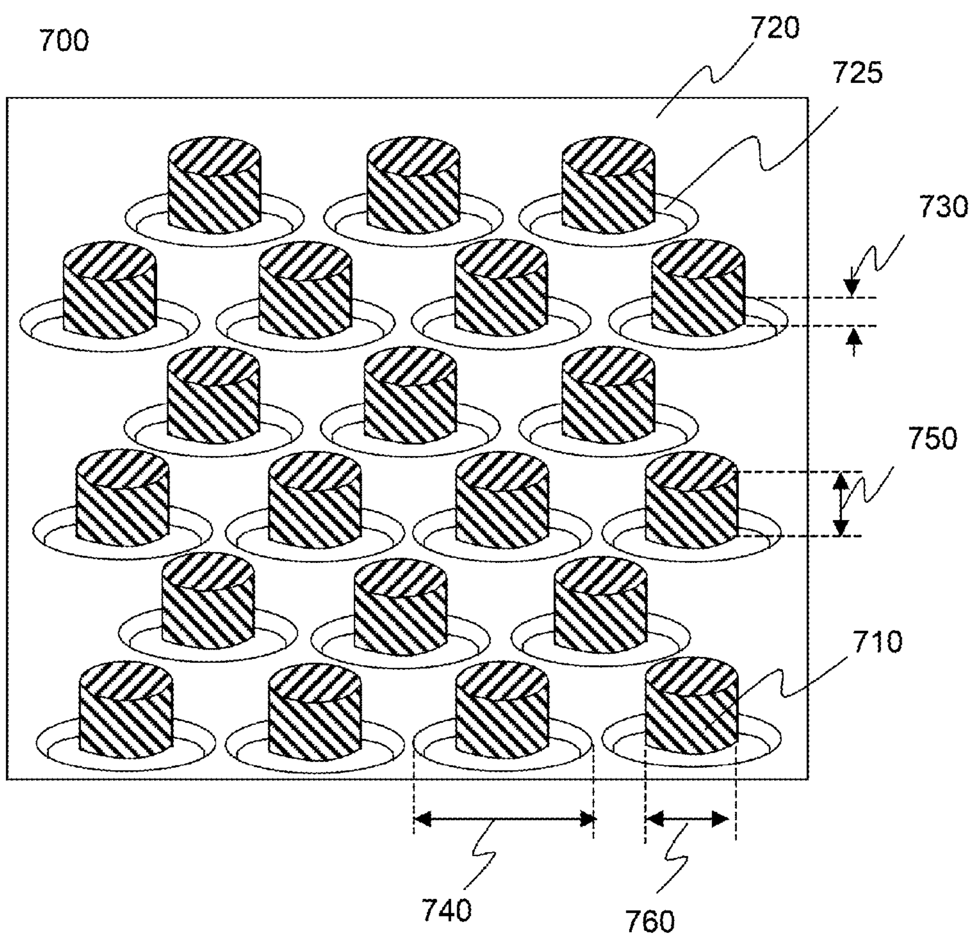



FIG. 7

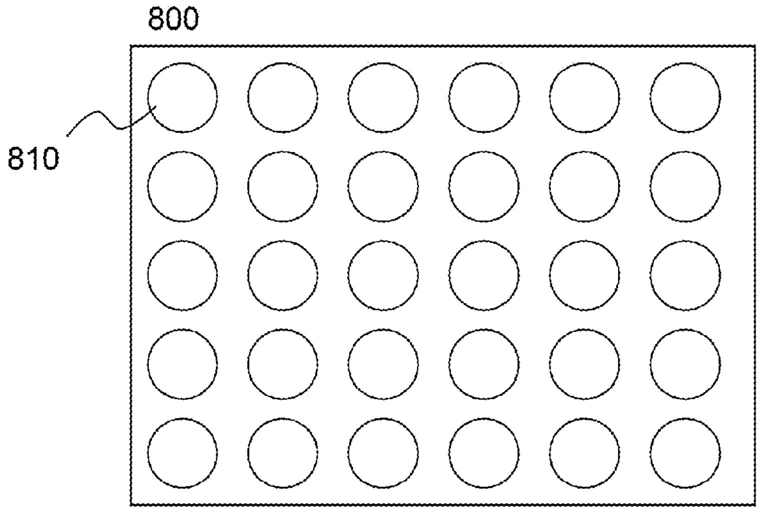



FIG. 8A

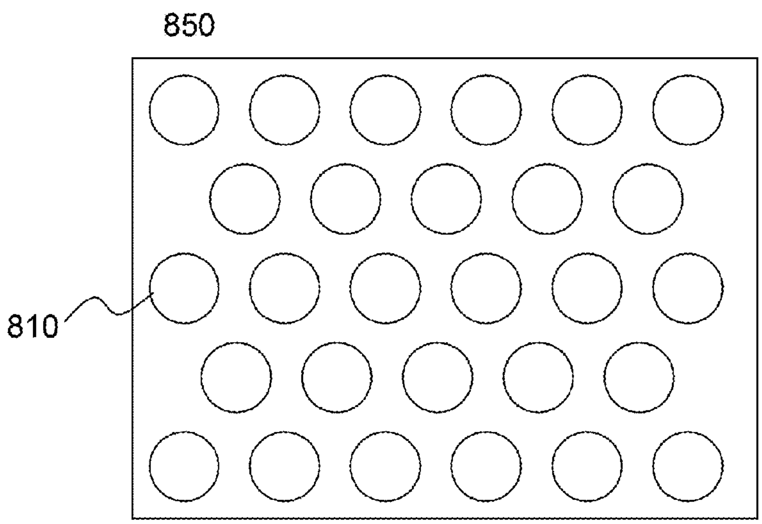



FIG. 8B

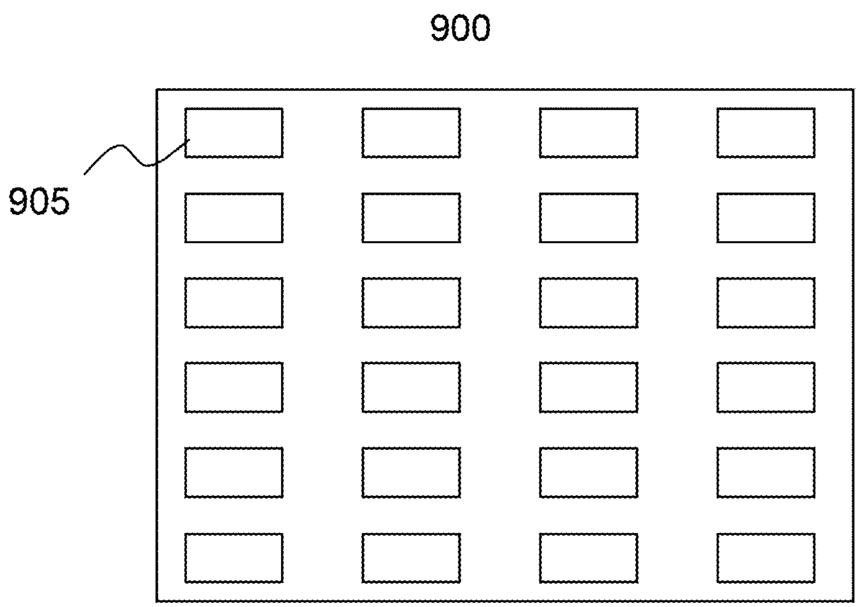



FIG. 9A

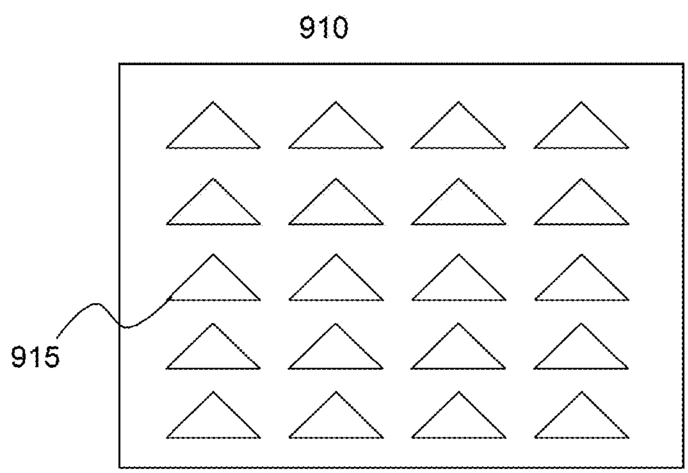



FIG. 9B

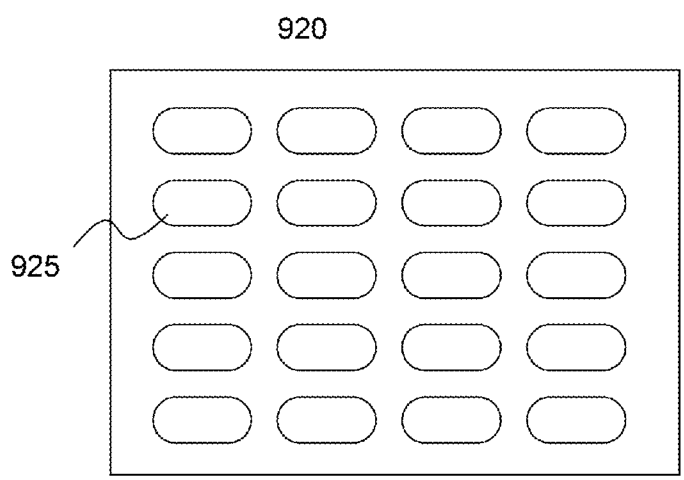



FIG. 9C

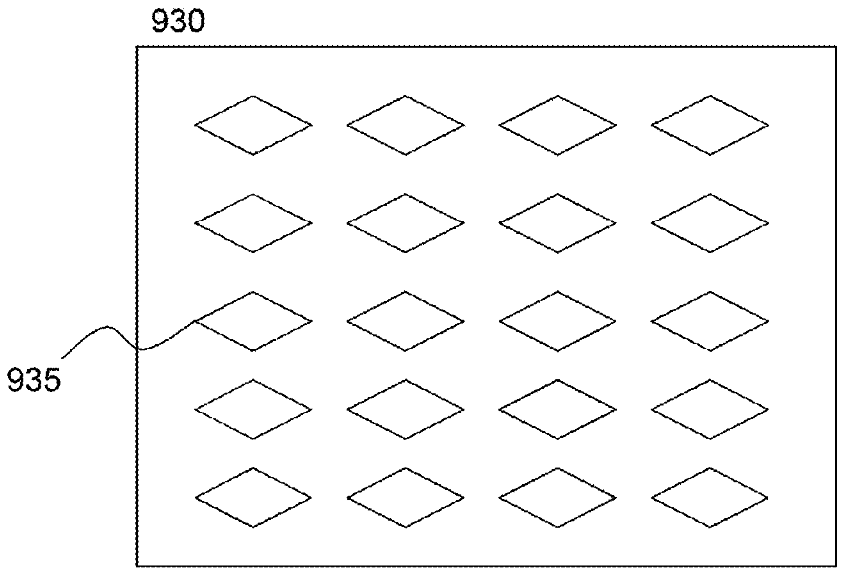



FIG. 9D

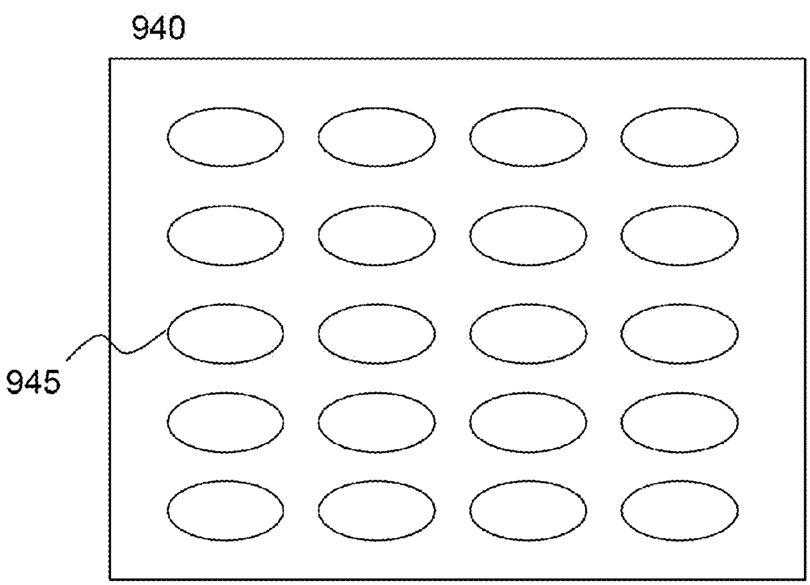



FIG. 9E

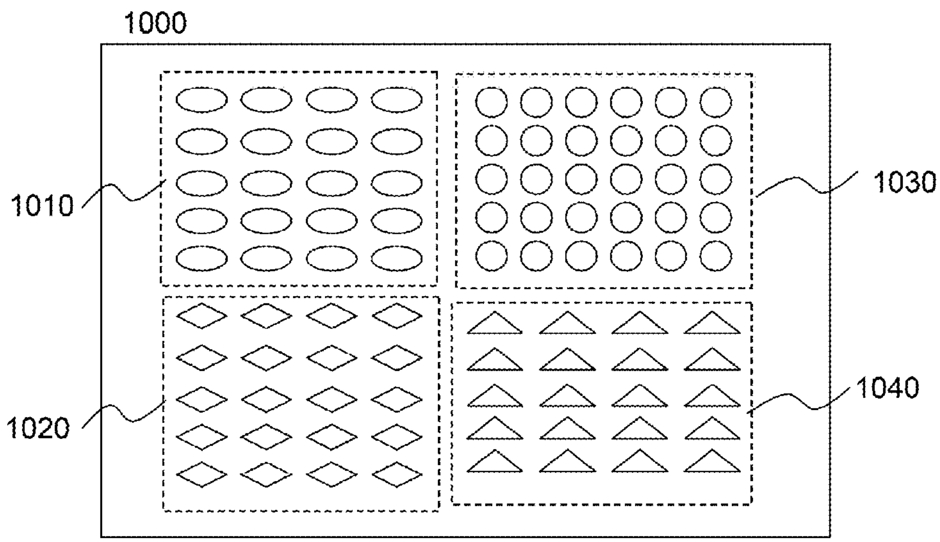



FIG. 10

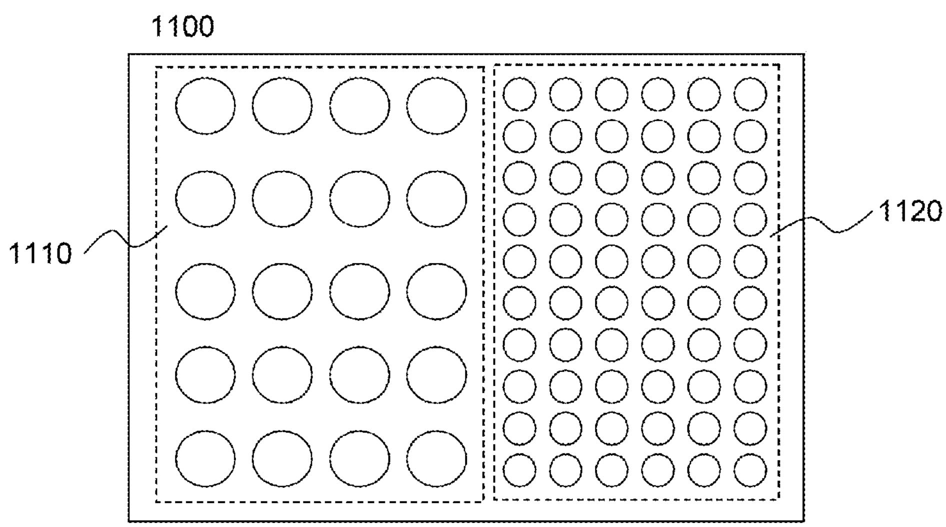



FIG. 11

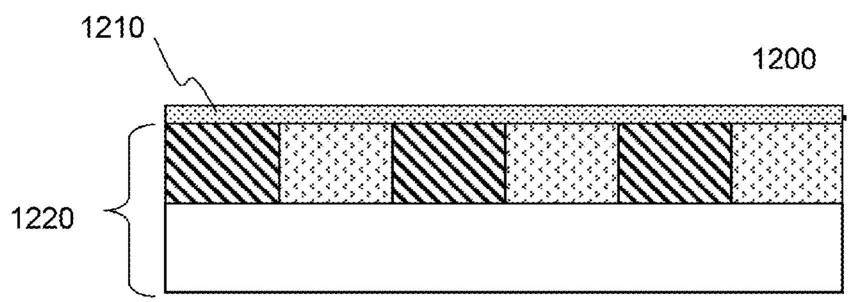



FIG. 12

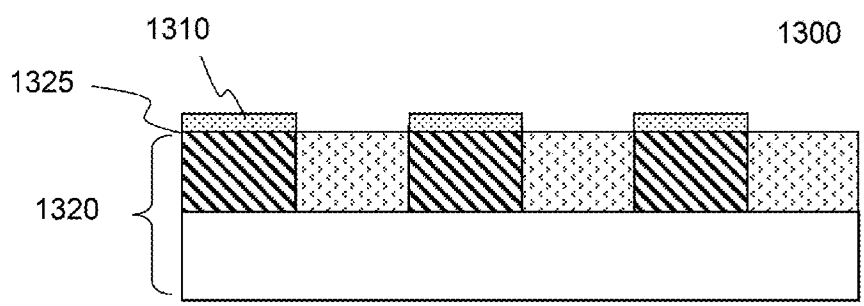



FIG. 13

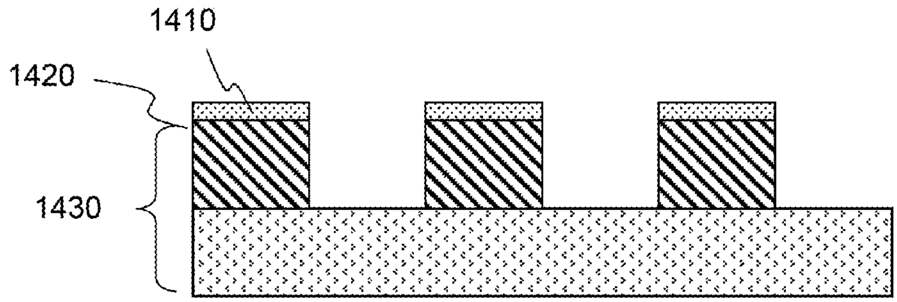



FIG. 14

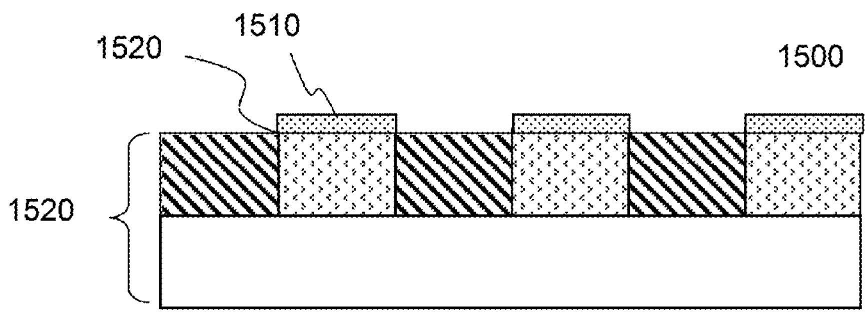



FIG. 15

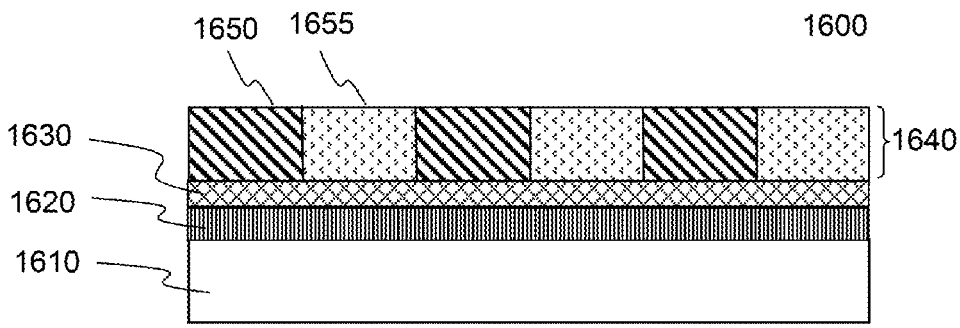



FIG. 16

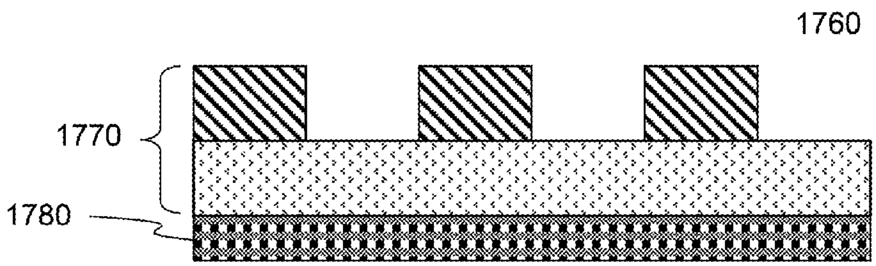



FIG. 17

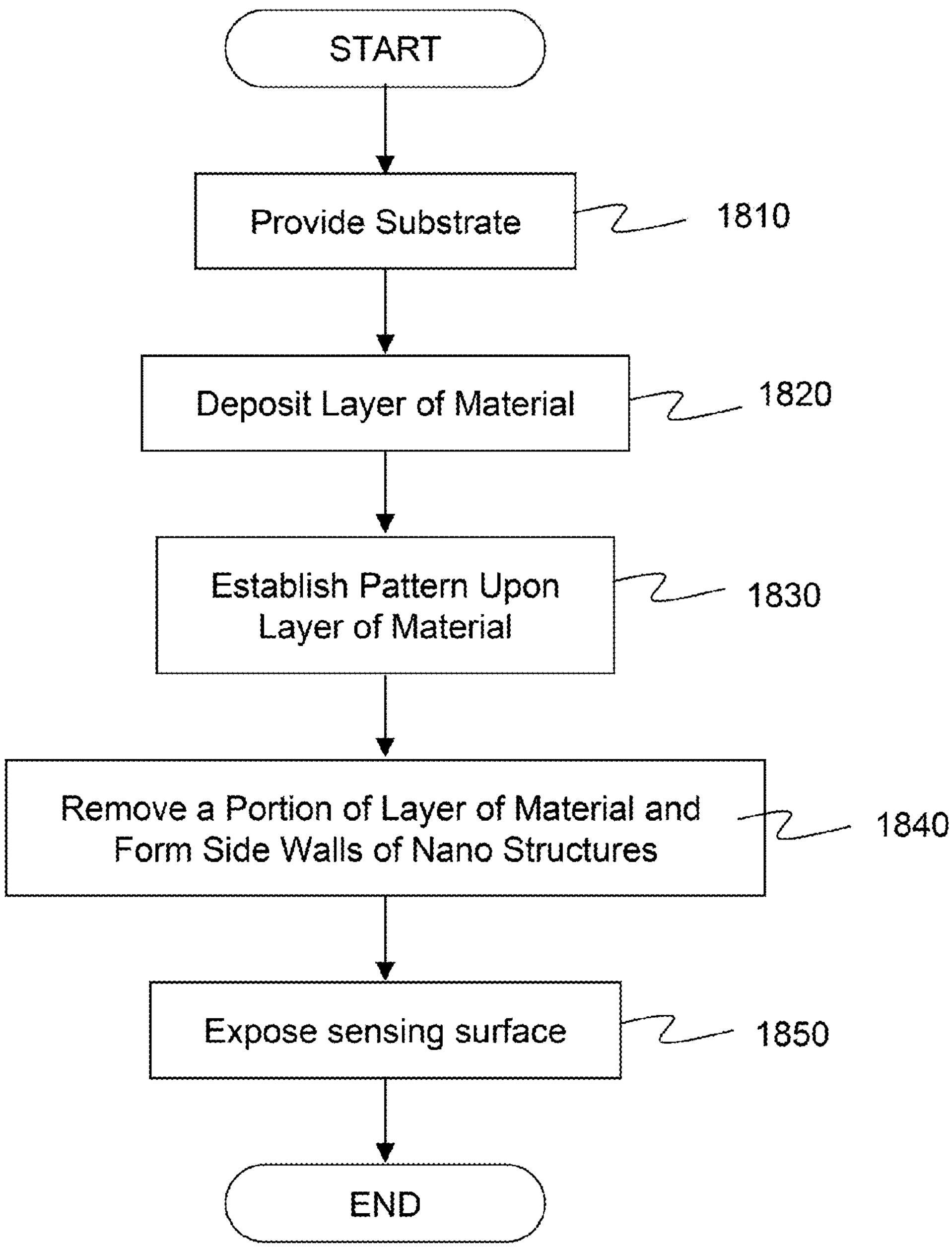

START
Provide Substrate
1810
Deposit Layer of Material
1820
Establish Pattern Upon Layer of Material
1830
Remove a Portion of Layer of Material and Form Side Walls of Nano Structures
1840
Expose sensing surface
1850
END

FIG. 18

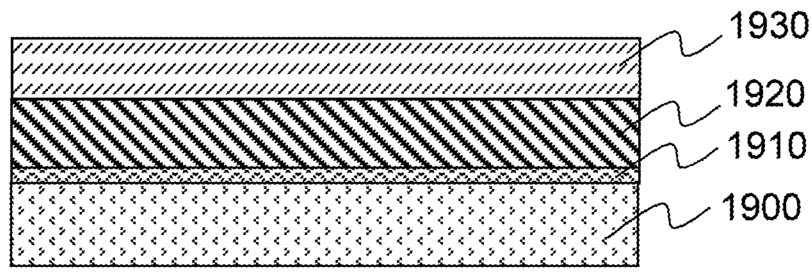



FIG. 19A

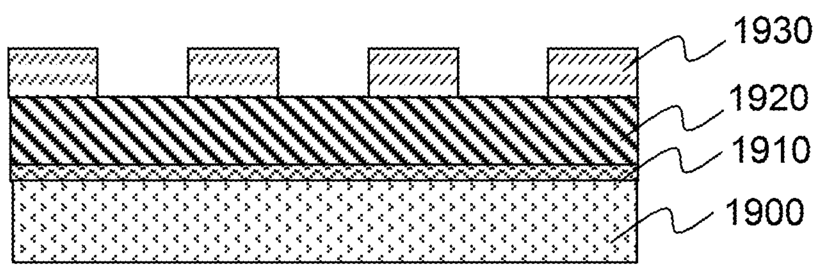



FIG. 19B

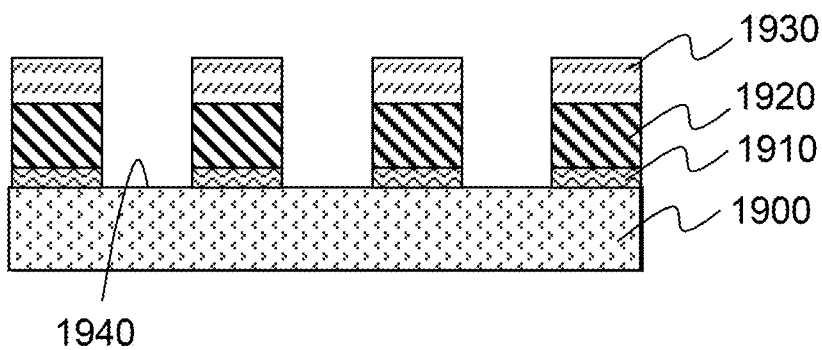



FIG. 19C

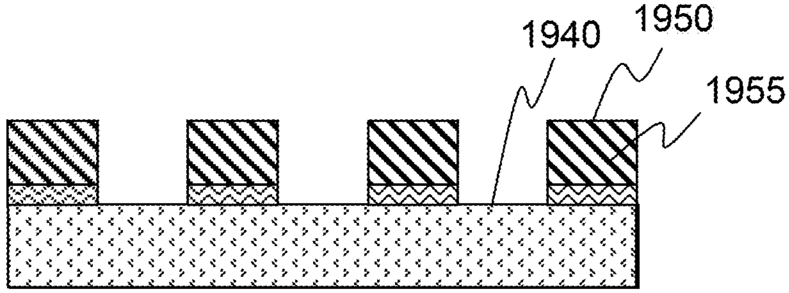



FIG. 19D

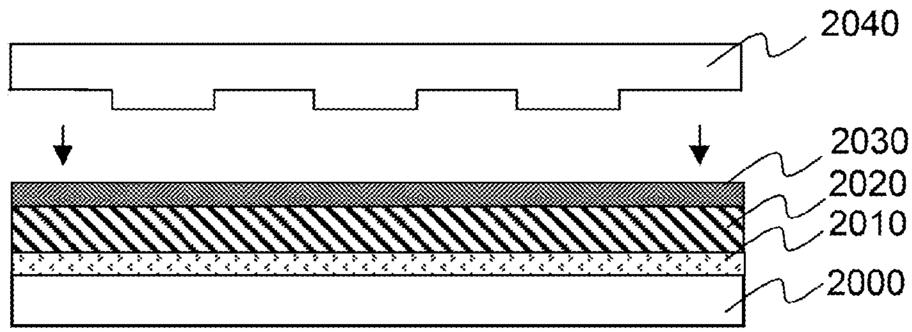



FIG. 20A

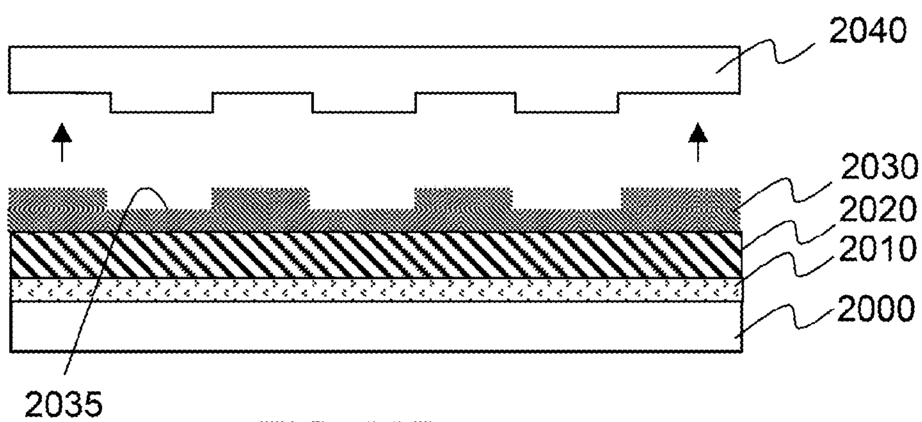



FIG. 20B

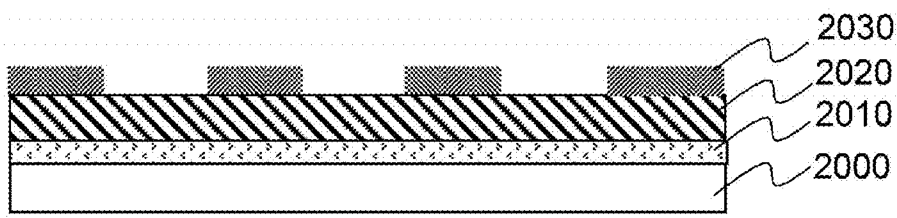



FIG. 20C

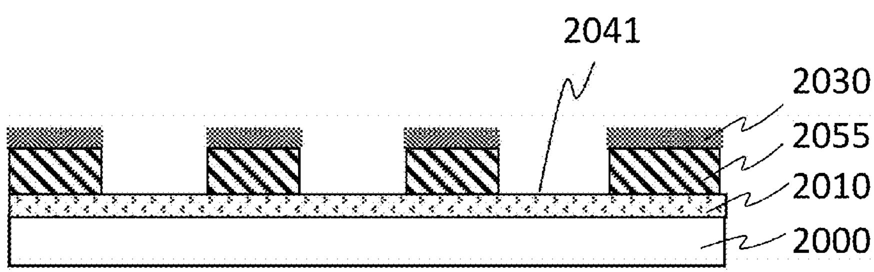



FIG. 20D

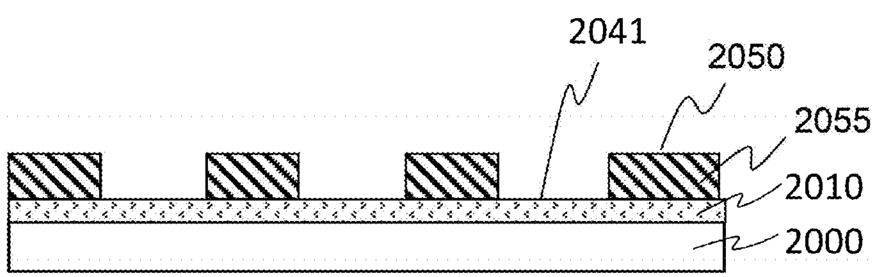



FIG. 20E

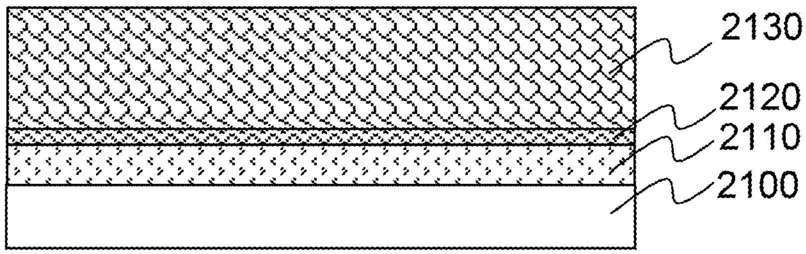



FIG. 21A

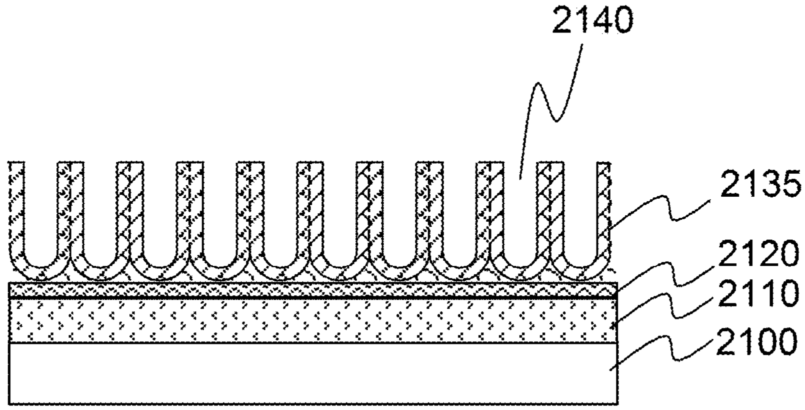



FIG. 21B

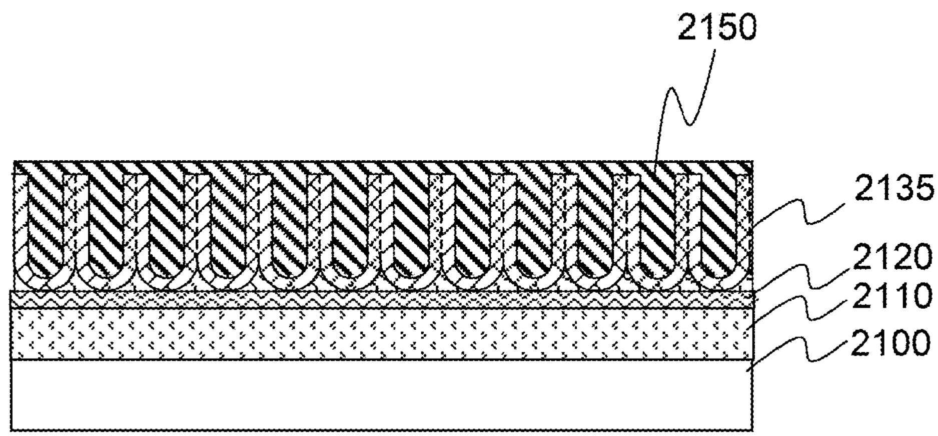



FIG. 21C

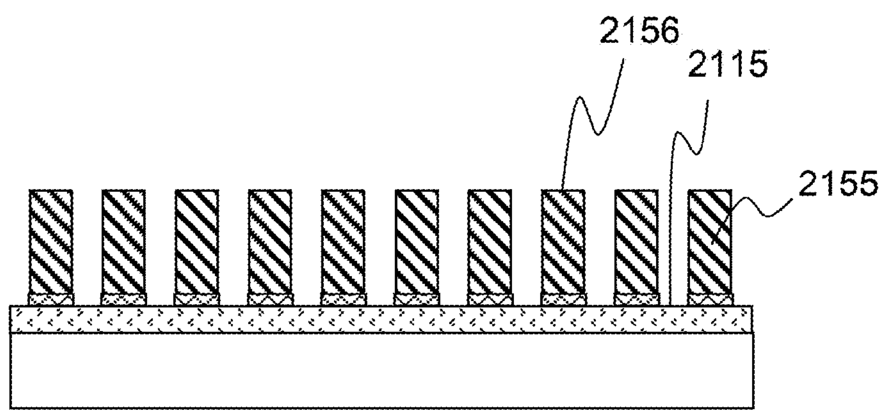



FIG. 21D

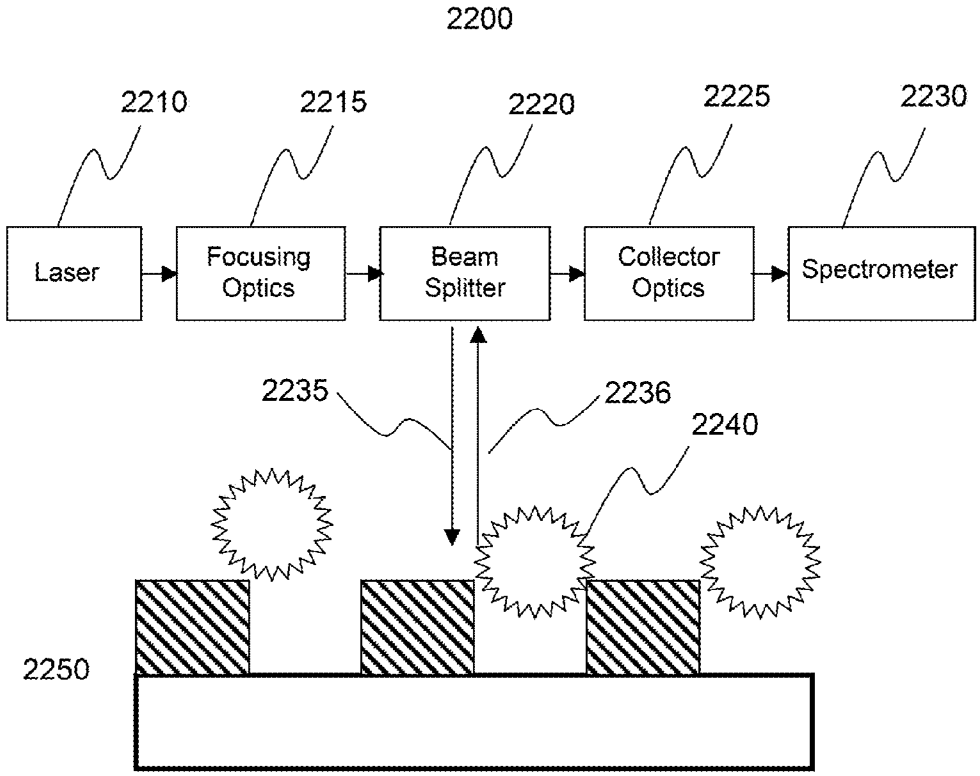

2200
2210
2215
2220
2225
2230
Laser
Focusing Optics
Beam Splitter
Collector Optics
Spectrometer
2235
2236
2240
2250

FIG. 22

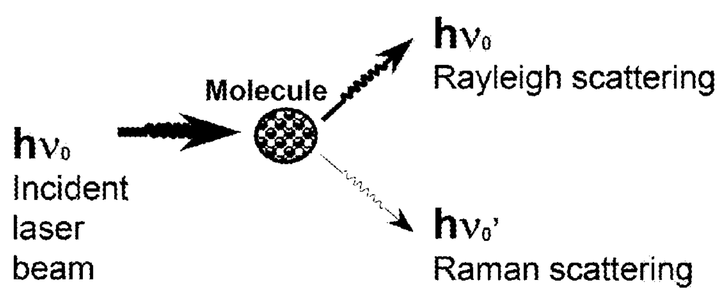



FIG. 23A

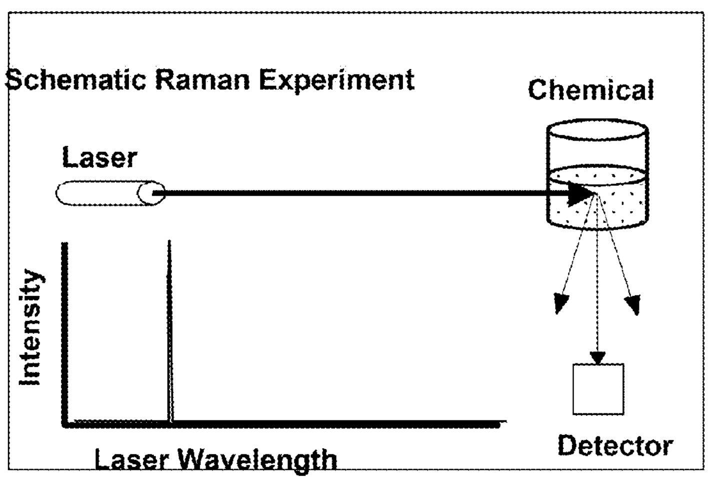



FIG. 23B

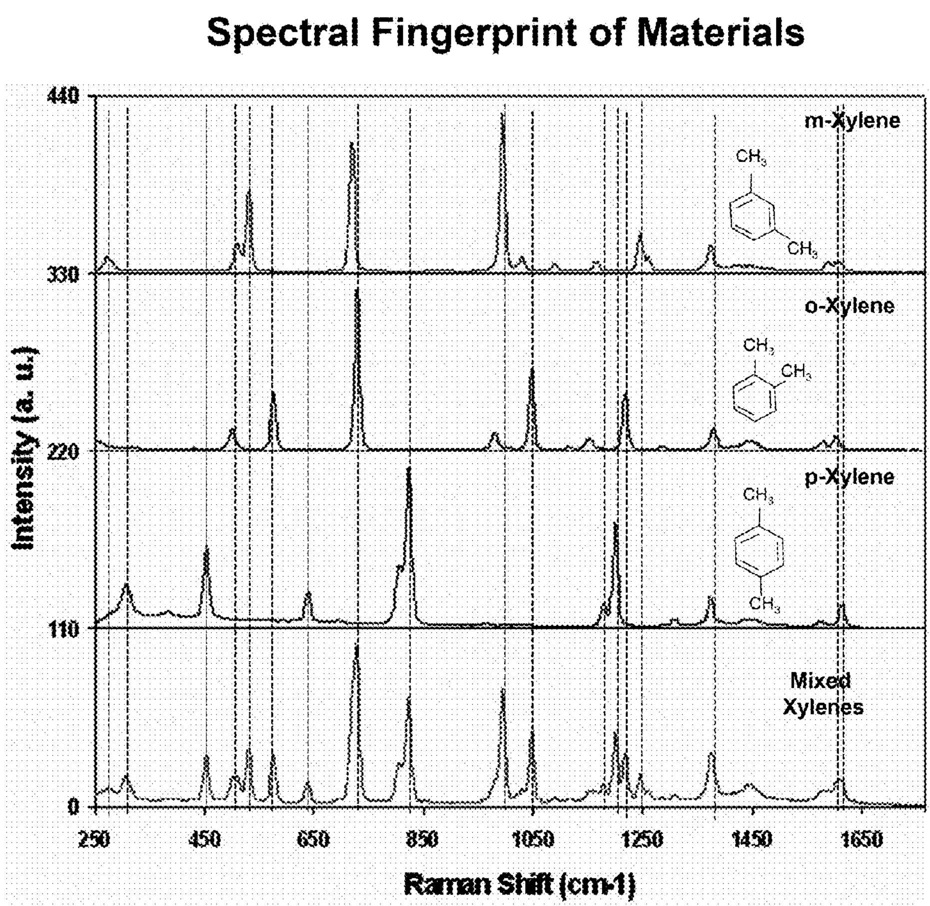

Spectral Fingerprint of Materials
m-Xylene
$CH_3$
$CH_3$
o-Xylene
$CH_3$
$CH_3$
p-Xylene
$CH_3$
$CH_3$
Mixed Xylenes
Intensity (a. u.)
440
330
220
110
0
250
450
650
850
1050
1250
1450
1650
Raman Shift (cm-1)

FIG. 23C

Schematic Top Views of SEM Micrographs

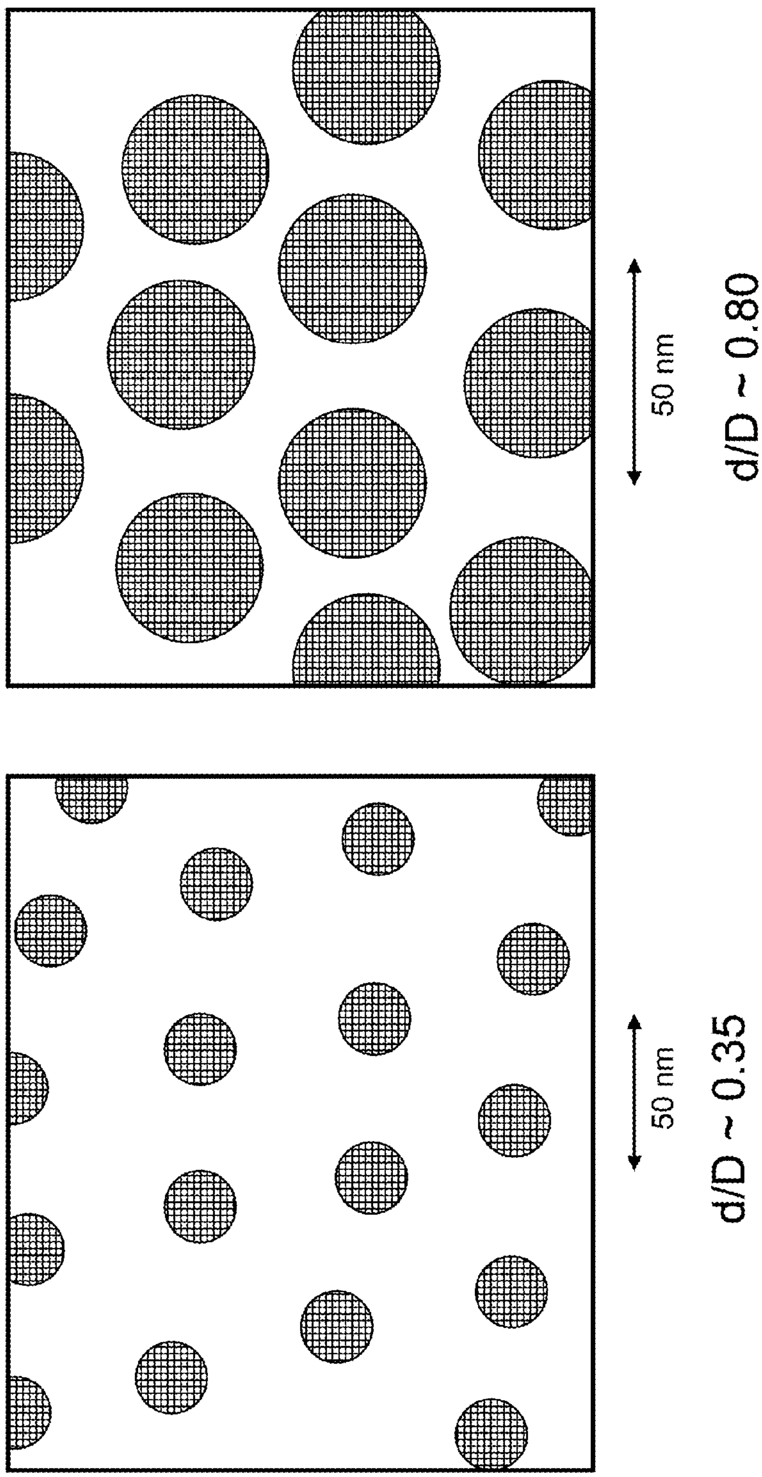



Figure 24

**SERS Spectra of Methamidophos**

Methamidophos (MAP): key pesticide; Nerve agent simulant

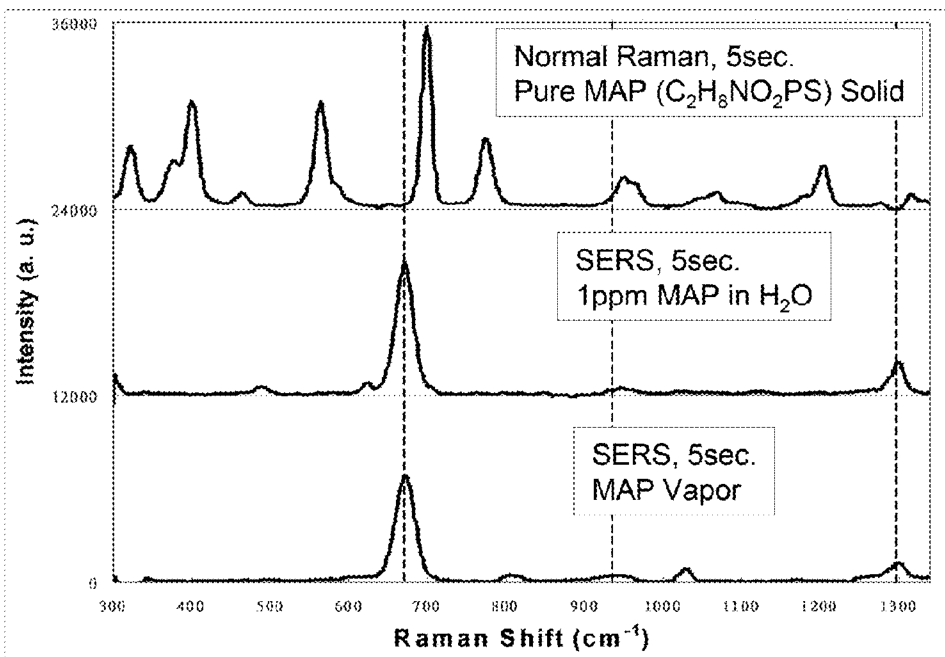



FIG. 25

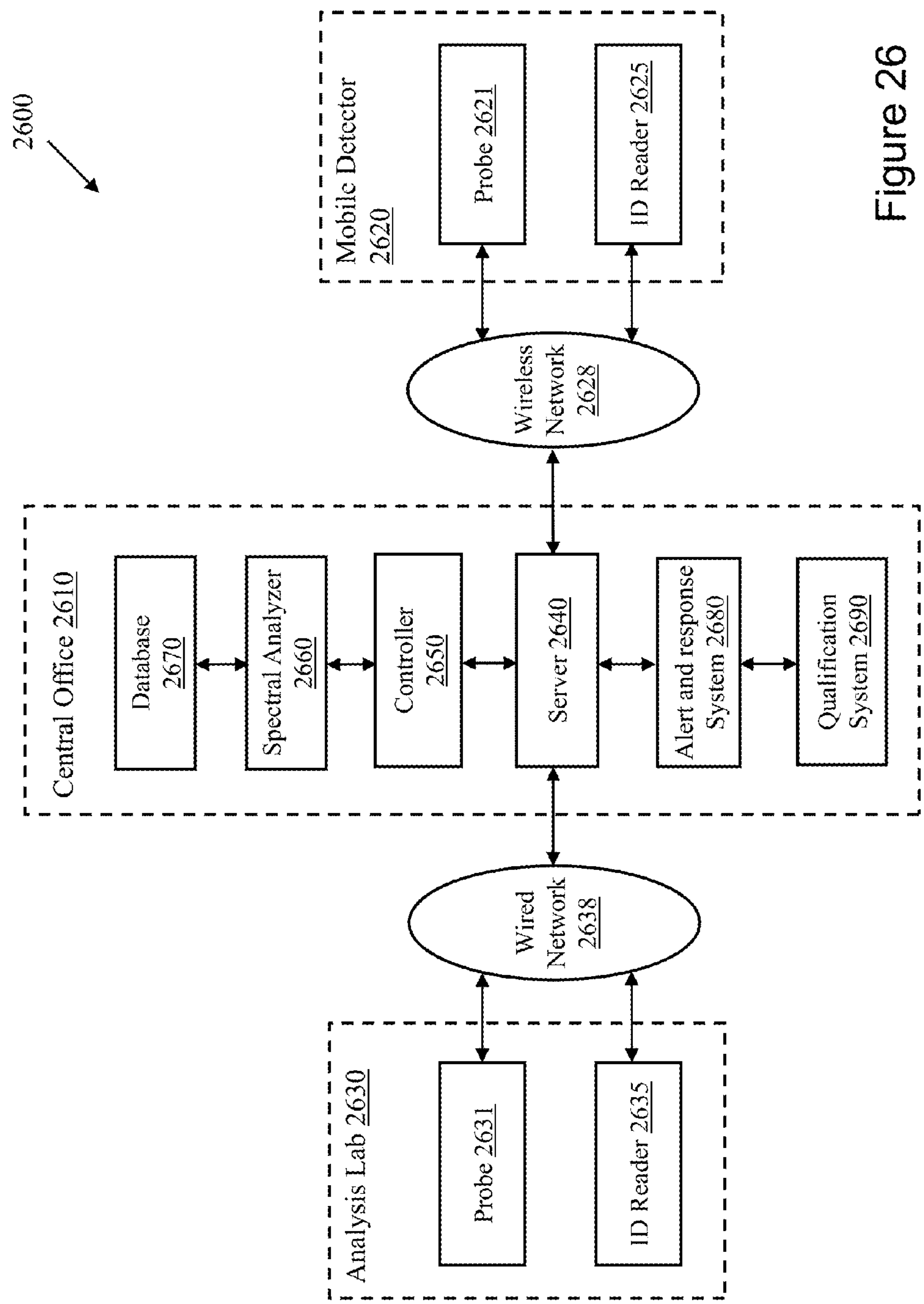

2600
Mobile Detector 2620
Probe 2621
ID Reader 2625
Wireless Network 2628
Central Office 2610
Database 2670
Spectral Analyzer 2660
Controller 2650
Server 2640
Alert and response System 2680
Qualification System 2690
Wired Network 2638
Analysis Lab 2630
Probe 2631
ID Reader 2635

Figure 26

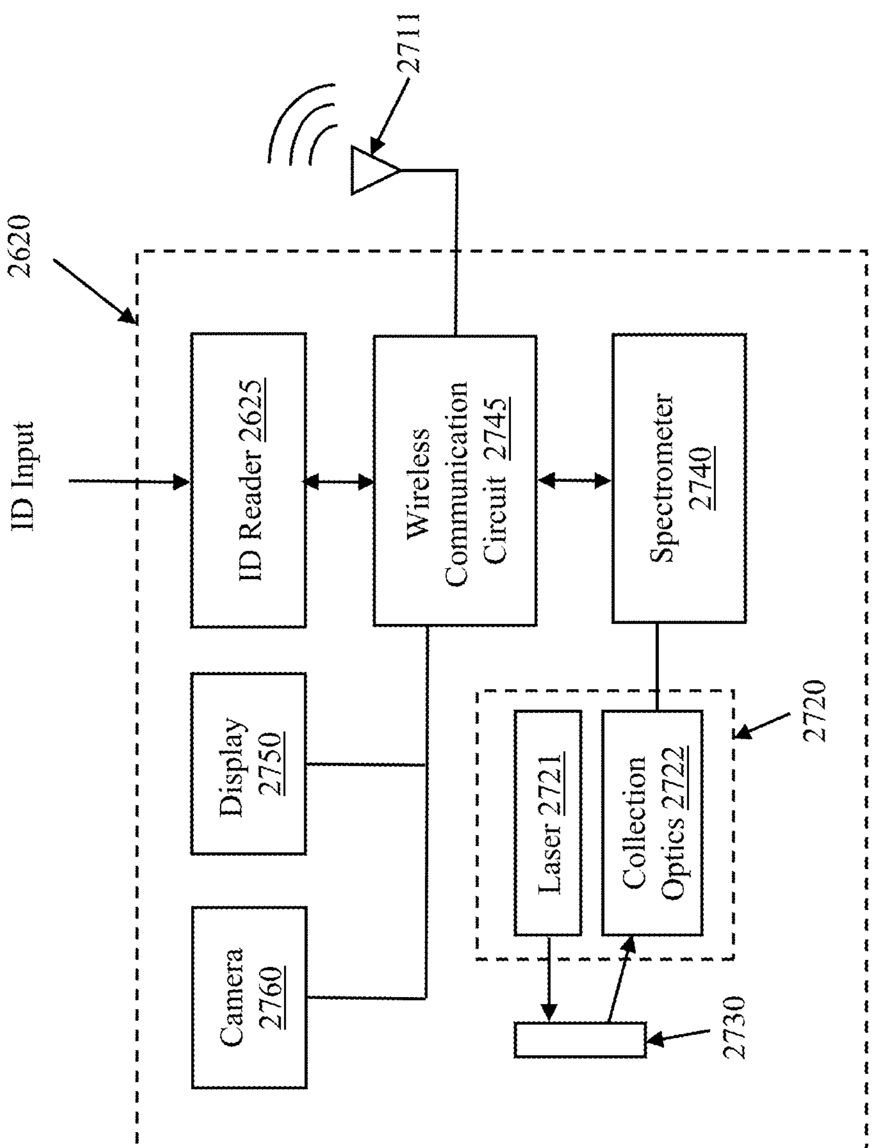

2711
2620
ID Input
ID Reader 2625
Wireless Communication Circuit 2745
Spectrometer 2740
Display 2750
Camera 2760
Laser 2721
Collection Optics 2722
2720
2730

Figure 27

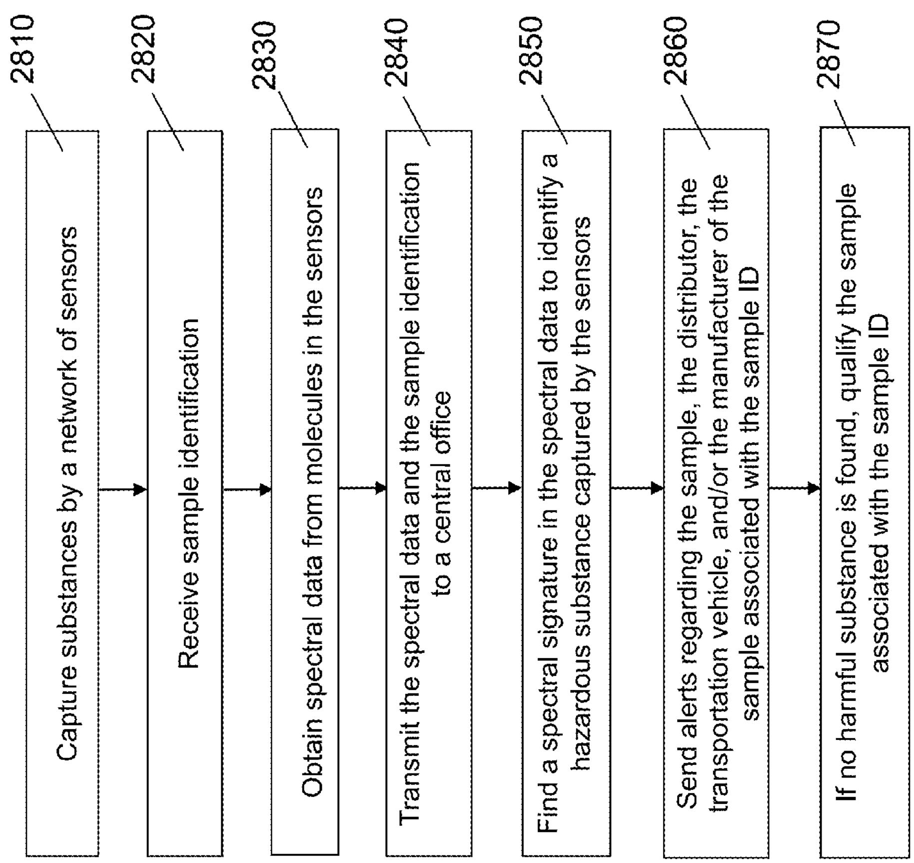

2810
Capture substances by a network of sensors
2820
Receive sample identification
2830
Obtain spectral data from molecules in the sensors
2840
Transmit the spectral data and the sample identification to a central office
2850
Find a spectral signature in the spectral data to identify a hazardous substance captured by the sensors
2860
Send alerts regarding the sample, the distributor, the transportation vehicle, and/or the manufacturer of the sample associated with the sample ID
2870
If no harmful substance is found, qualify the sample associated with the sample ID

Figure 28

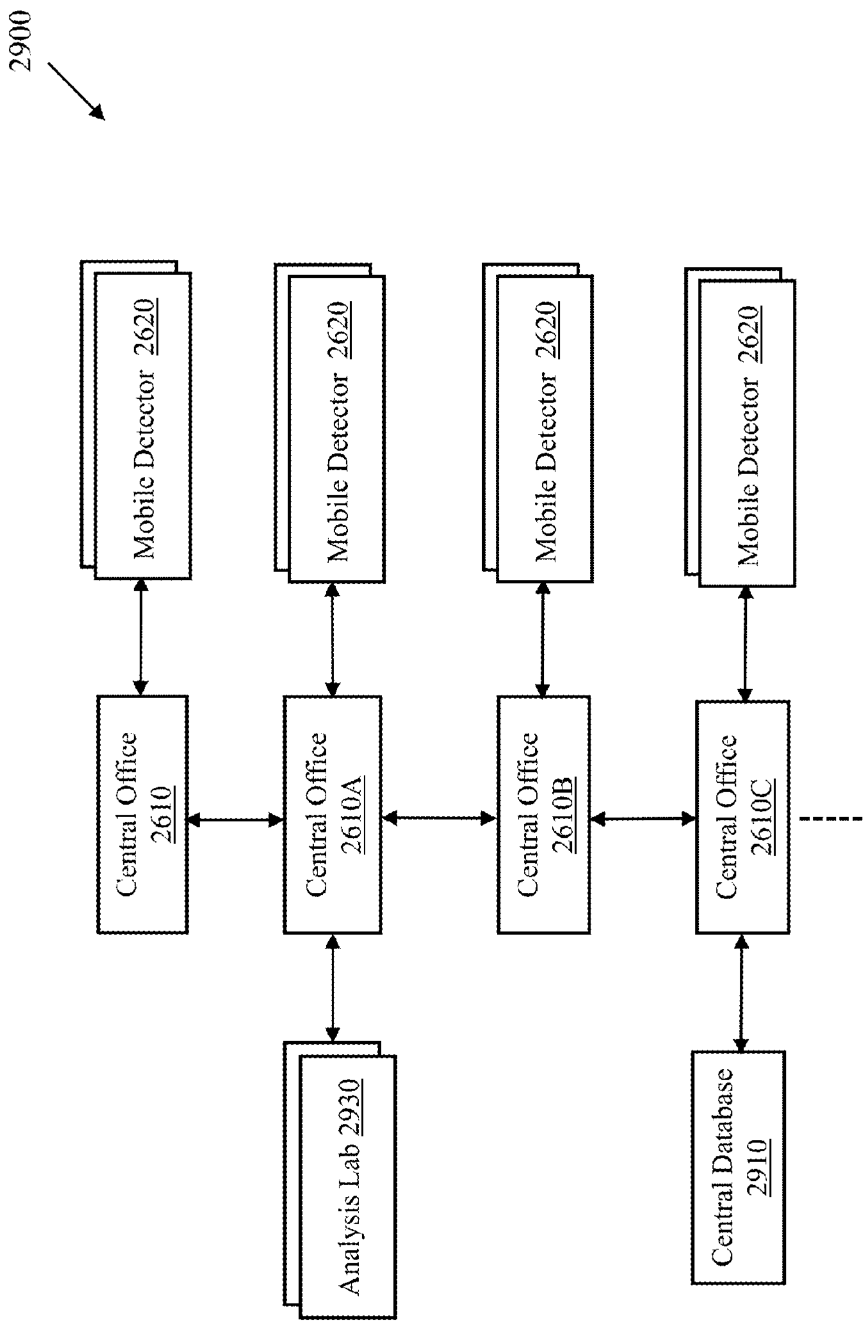

2900
Mobile Detector 2620
Mobile Detector 2620
Mobile Detector 2620
Mobile Detector 2620
Central Office 2610
Central Office 2610A
Central Office 2610B
Central Office 2610C
Analysis Lab 2930
Central Database 2910

Figure 29

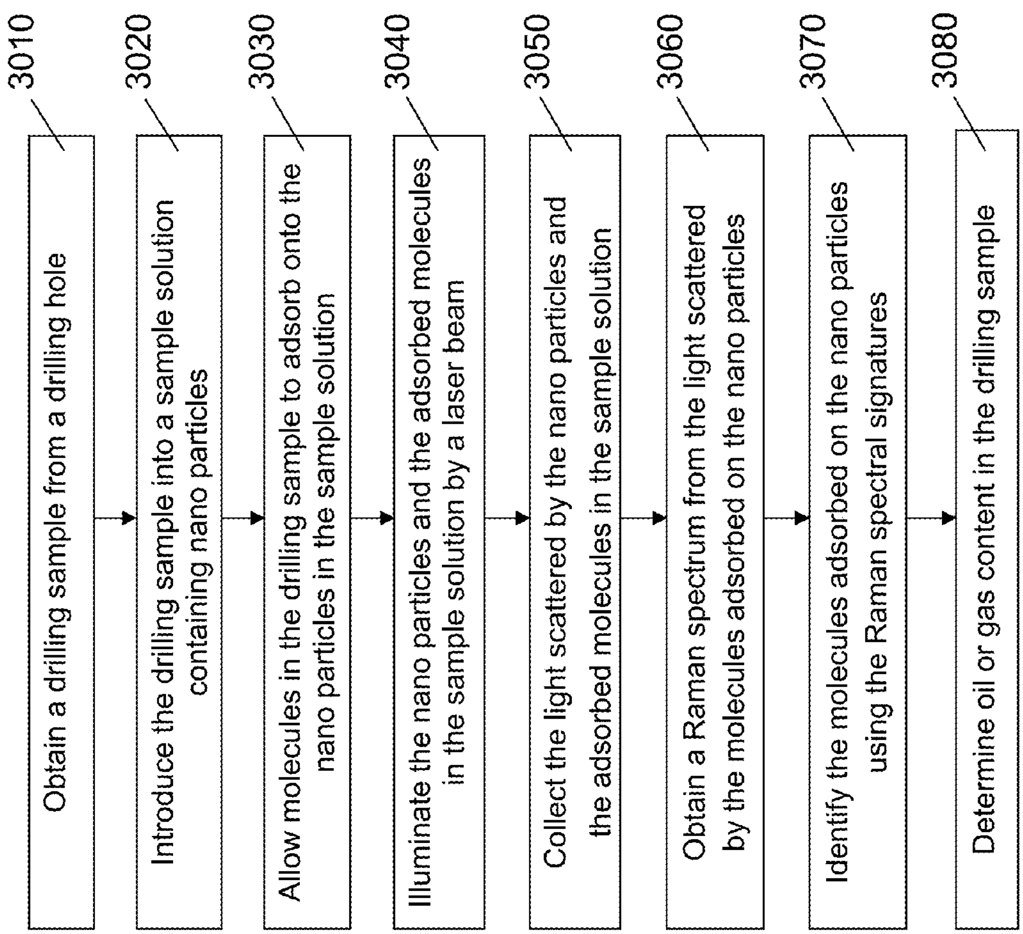

3010
Obtain a drilling sample from a drilling hole
3020
Introduce the drilling sample into a sample solution containing nano particles
3030
Allow molecules in the drilling sample to adsorb onto the nano particles in the sample solution
3040
Illuminate the nano particles and the adsorbed molecules in the sample solution by a laser beam
3050
Collect the light scattered by the nano particles and the adsorbed molecules in the sample solution
3060
Obtain a Raman spectrum from the light scattered by the molecules adsorbed on the nano particles
3070
Identify the molecules adsorbed on the nano particles using the Raman spectral signatures
3080
Determine oil or gas content in the drilling sample

Figure 30

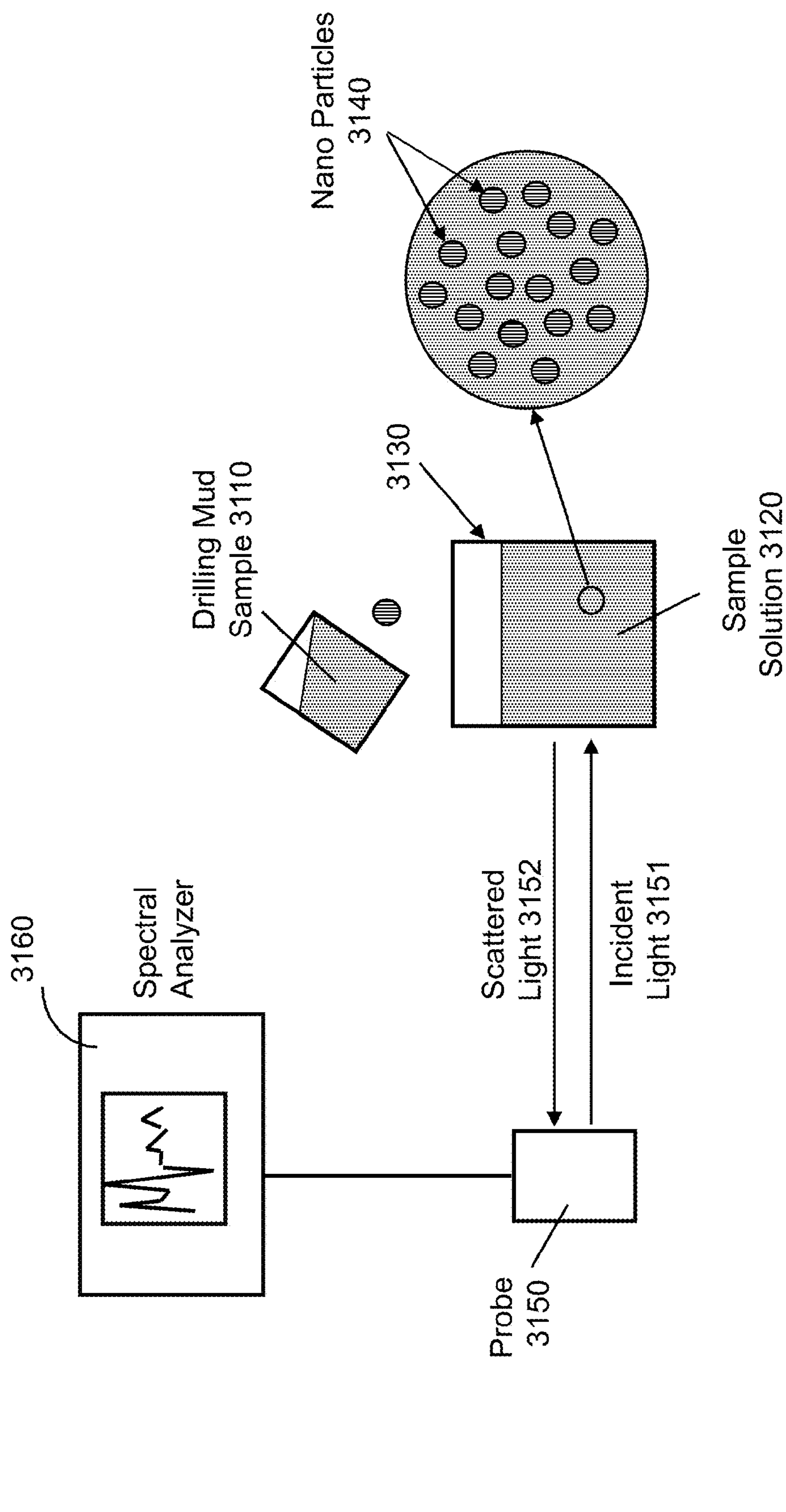

Nano Particles
3140
Drilling Mud
Sample 3110
3130
Sample
Solution 3120
3160
Spectral
Analyzer
Scattered
Light 3152
Incident
Light 3151
Probe
3150

Figure 31

Schematic Top Views of SEM Micrographs

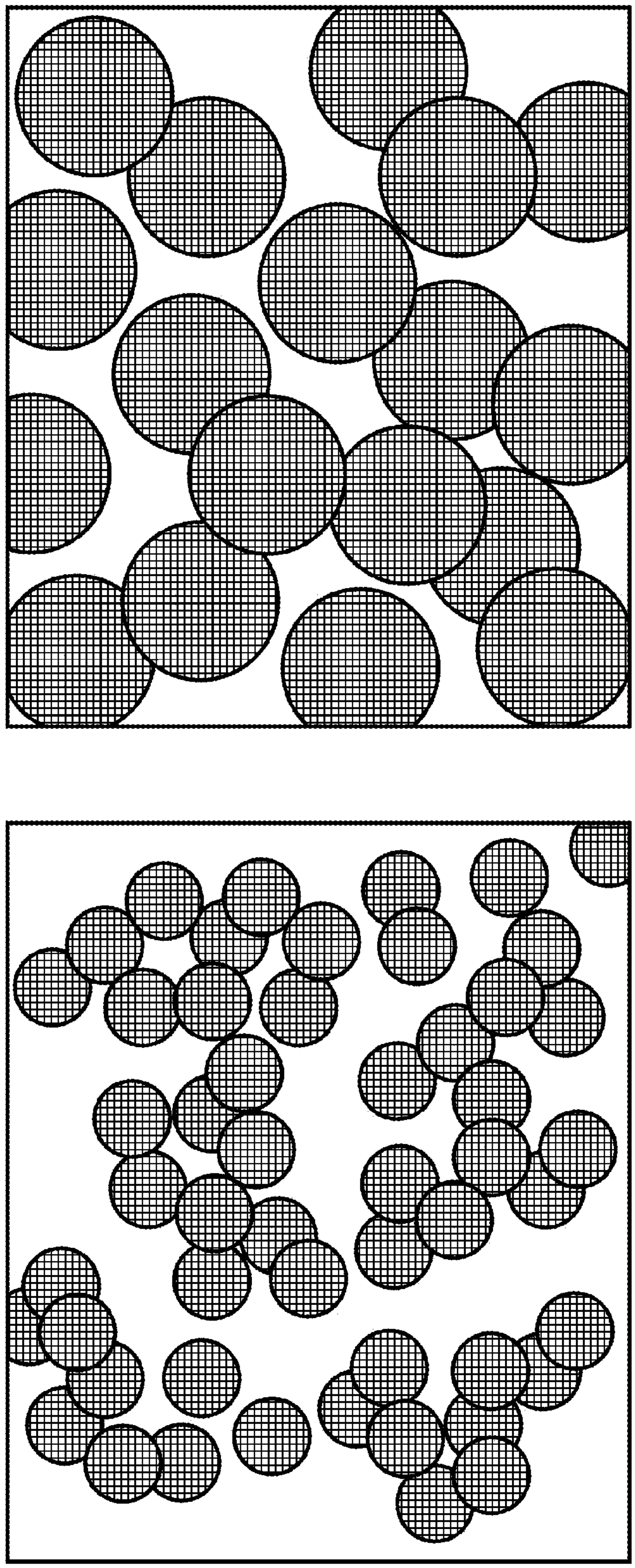


Figure 32

**Exemplified Size Distribution of Nano Particles**

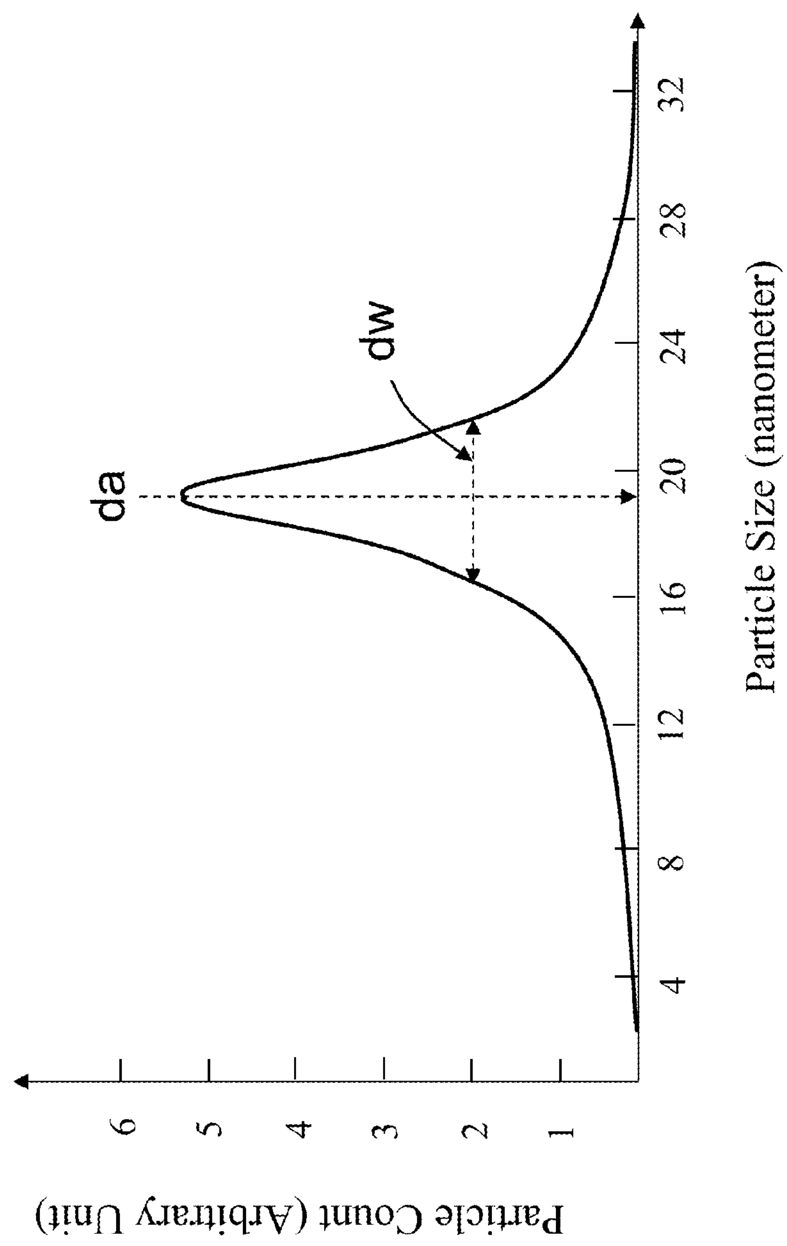



Figure 33

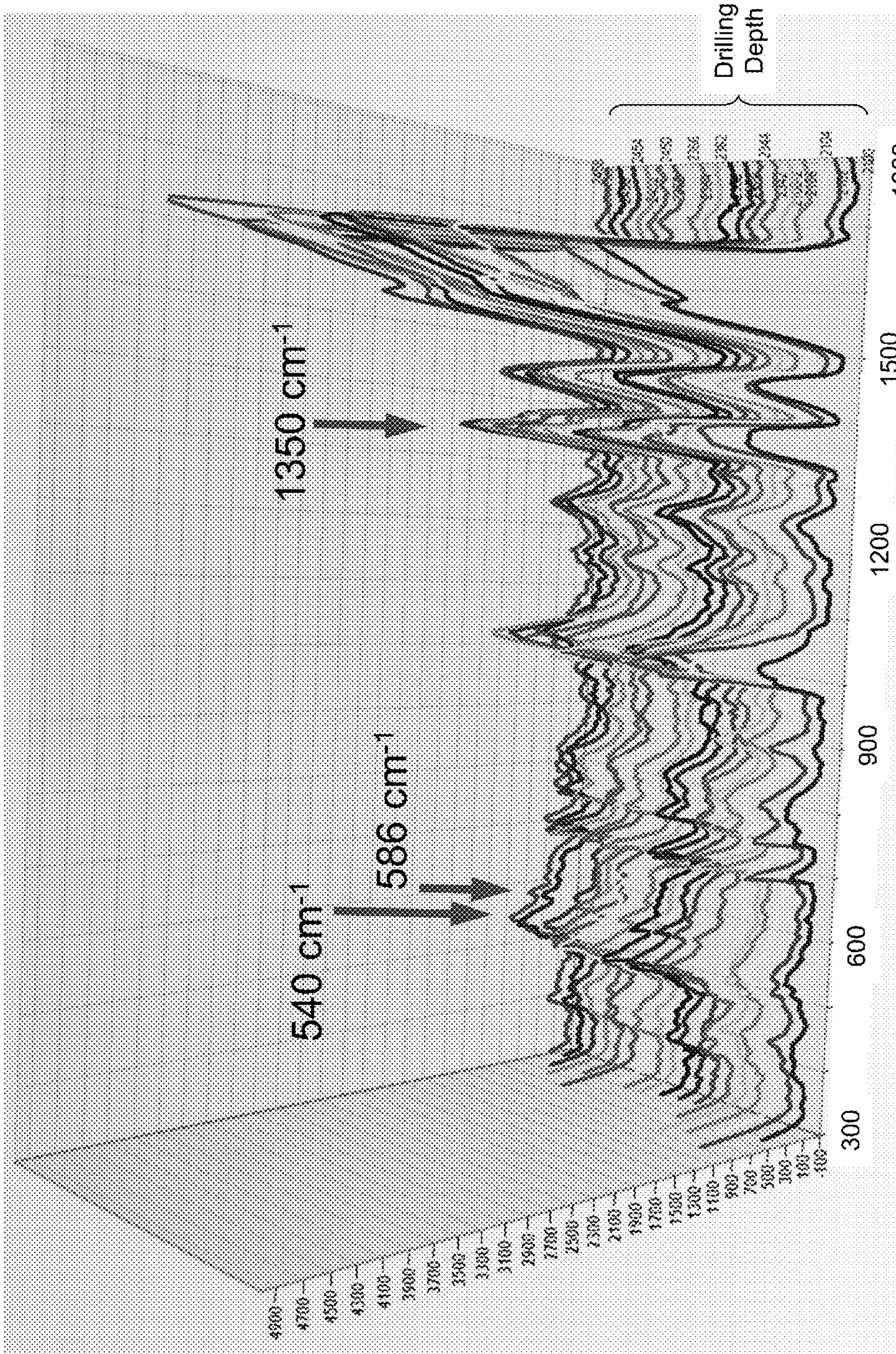

Drilling Depth
1350 cm$^{-1}$
540 cm$^{-1}$
586 cm$^{-1}$
300
600
900
1200
1500
1800
Raman Shift (cm$^{-1}$)

Figure 34

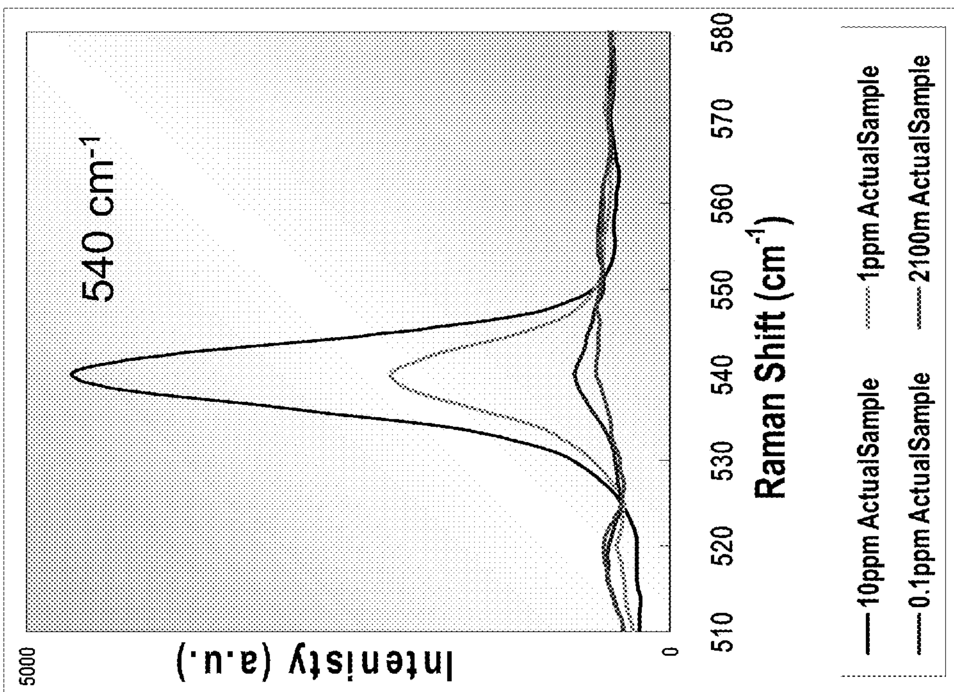

540 cm-1
Intenisty (a.u.)
5000
0
510
520
530
540
550
560
570
580
Raman Shift (cm-1)
10ppm ActualSample
1ppm ActualSample
0.1ppm ActualSample
2100m ActualSample

Figure 35A

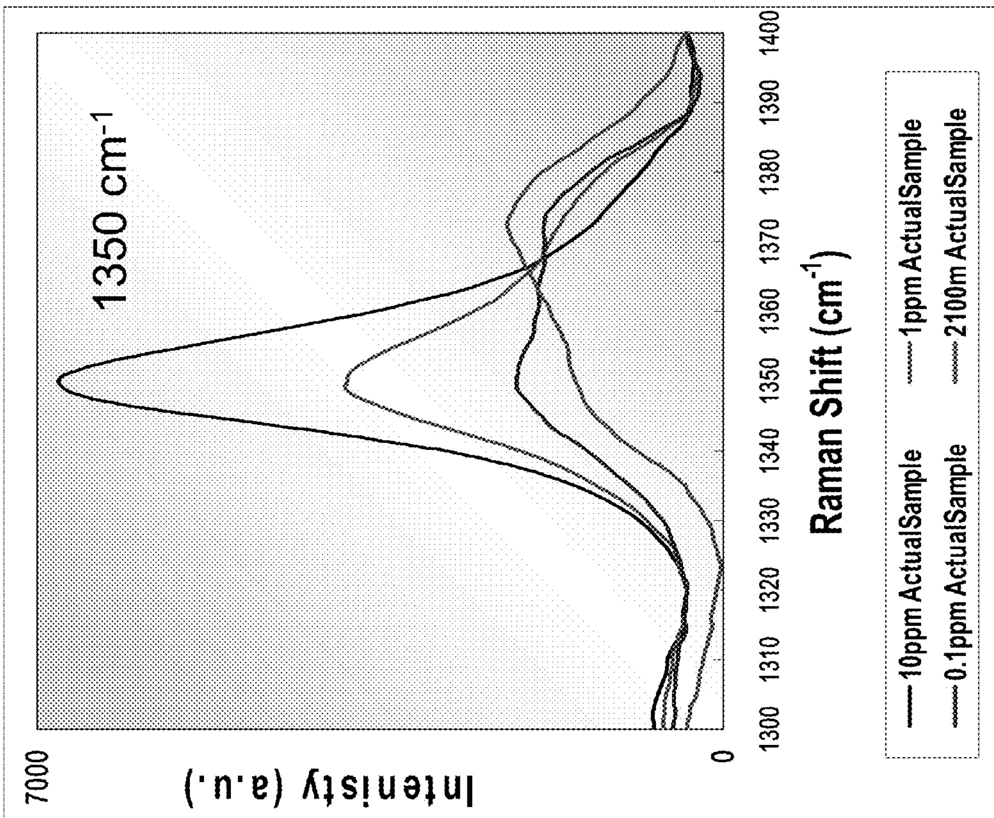
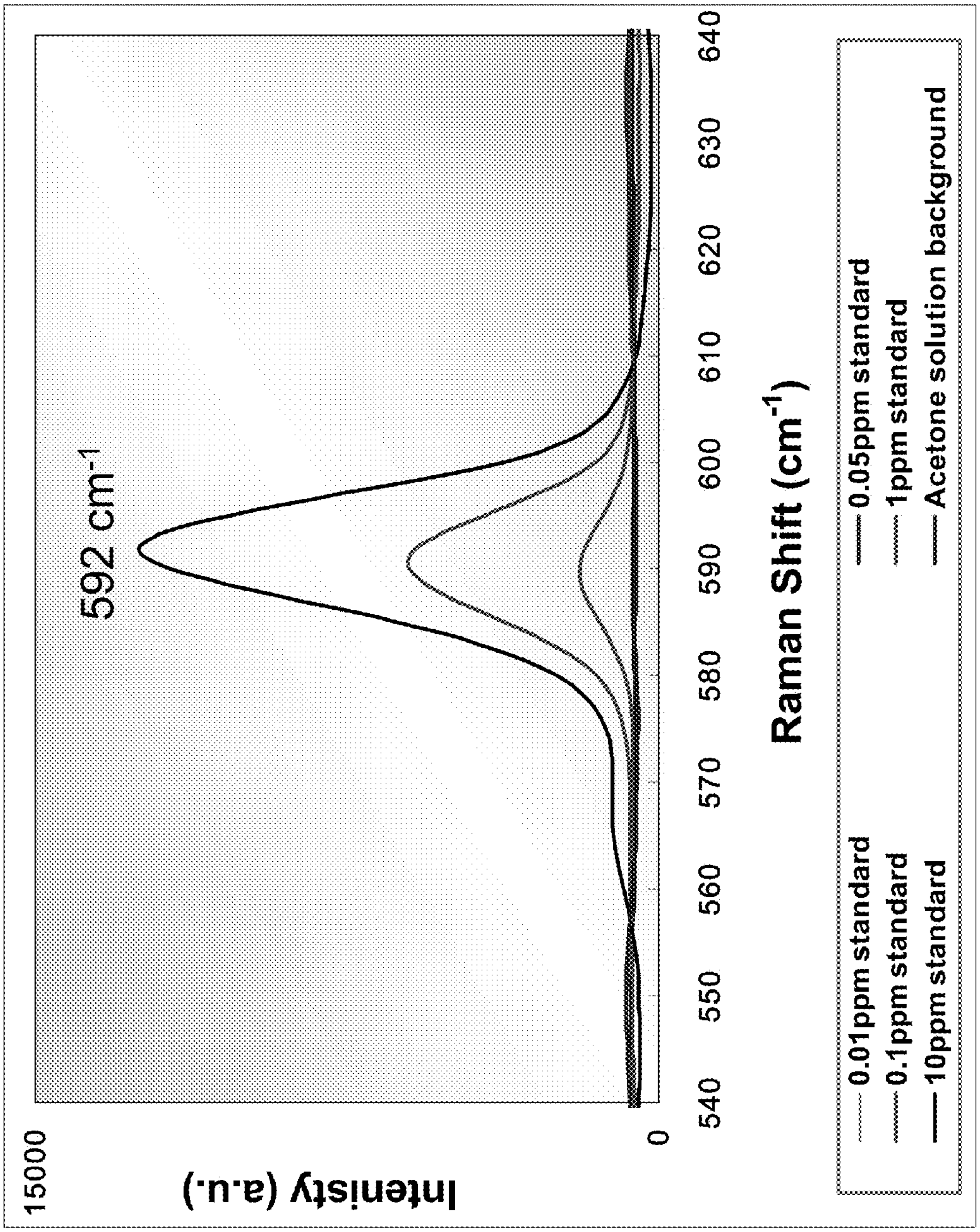

1350 cm-1
Intenisty (a.u.)
7000
0
1300
1310
1320
1330
1340
1350
1360
1370
1380
1390
1400
Raman Shift (cm-1)
10ppm ActualSample
1ppm ActualSample
0.1ppm ActualSample
2100m ActualSample

Figure 35B



592 cm-1
15000
0
Intenisty (a.u.)
540
550
560
570
580
590
600
610
620
630
640
Raman Shift (cm-1)
0.01ppm standard
0.1ppm standard
10ppm standard
0.05ppm standard
1ppm standard
Acetone solution background


Figure 35C

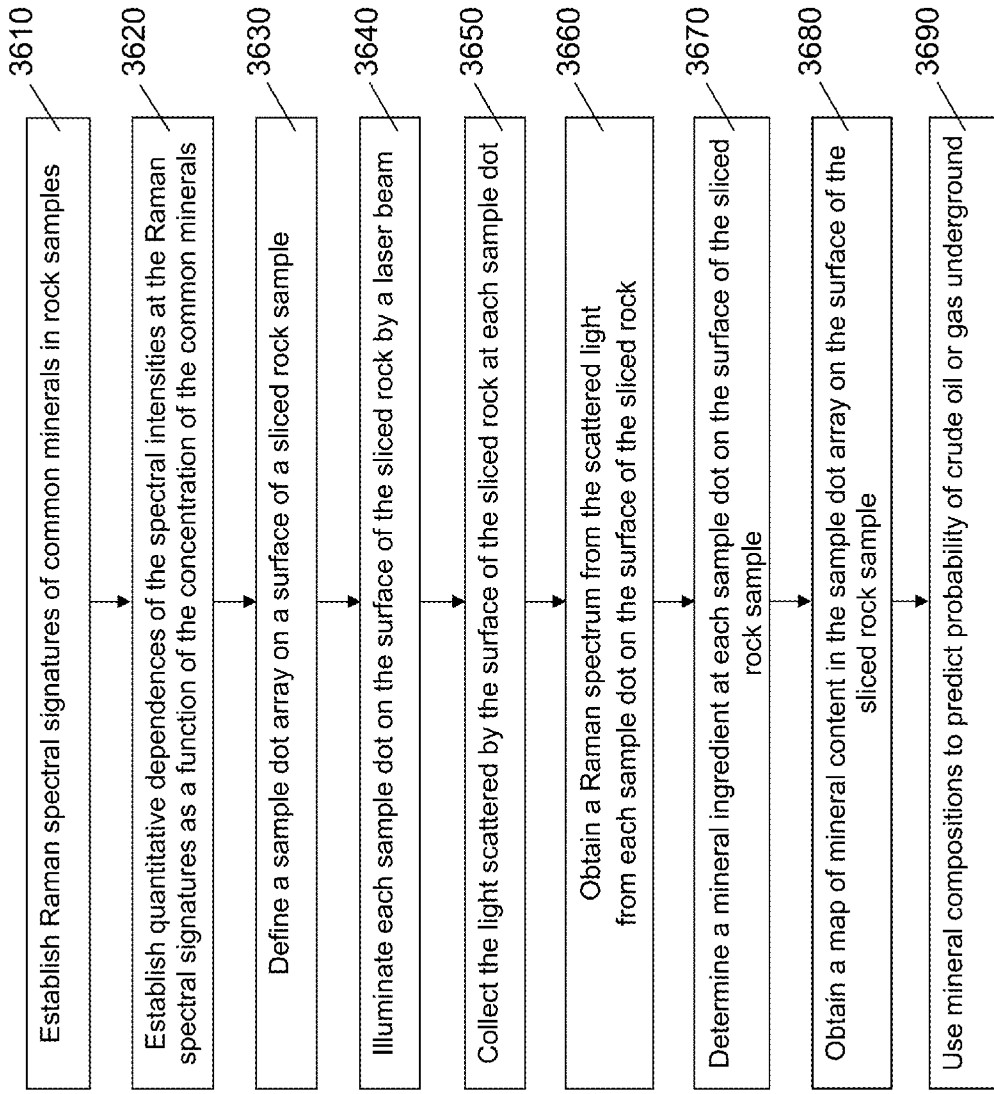

3610
Establish Raman spectral signatures of common minerals in rock samples
3620
Establish quantitative dependences of the spectral intensities at the Raman spectral signatures as a function of the concentration of the common minerals
3630
Define a sample dot array on a surface of a sliced rock sample
3640
Illuminate each sample dot on the surface of the sliced rock by a laser beam
3650
Collect the light scattered by the surface of the sliced rock at each sample dot
3660
Obtain a Raman spectrum from the scattered light from each sample dot on the surface of the sliced rock
3670
Determine a mineral ingredient at each sample dot on the surface of the sliced rock sample
3680
Obtain a map of mineral content in the sample dot array on the surface of the sliced rock sample
3690
Use mineral compositions to predict probability of crude oil or gas underground

Figure 36

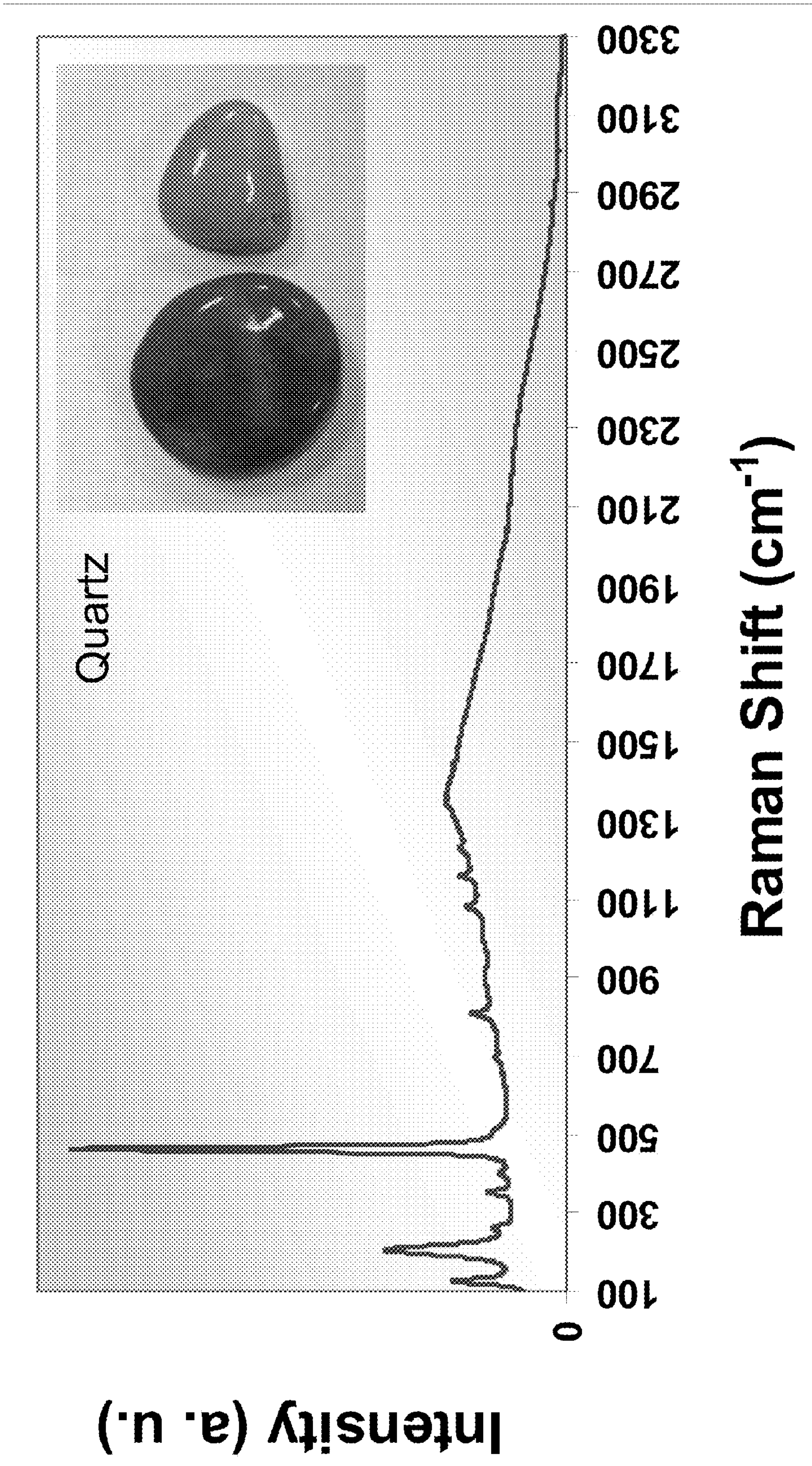

Quartz
Intensity (a. u.)
0
100
300
500
700
900
1100
1300
1500
1700
1900
2100
2300
2500
2700
2900
3100
3300
Raman Shift ($cm^{-1}$)

Figure 37A

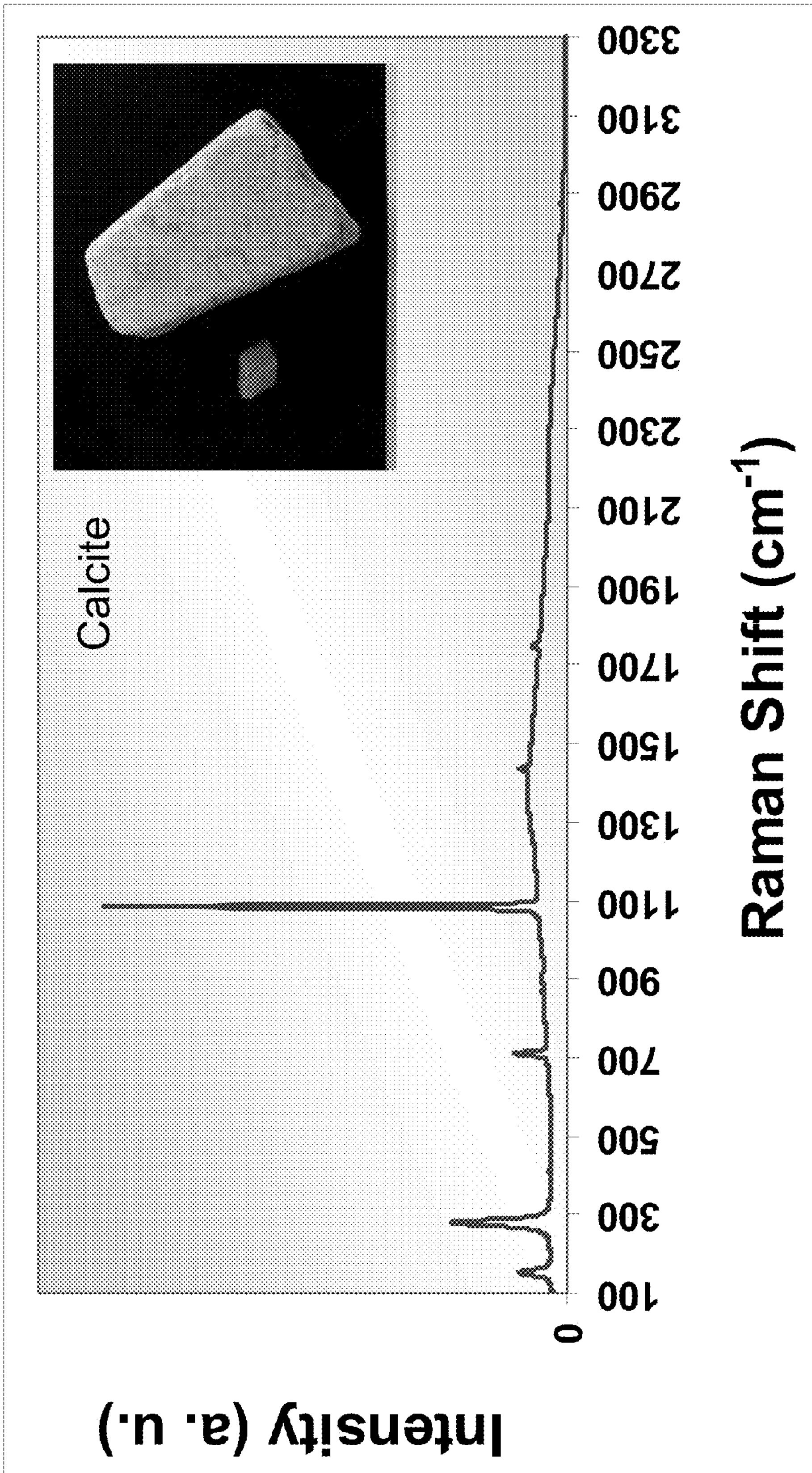

Calcite
Intensity (a. u.)
0
Raman Shift (cm$^{-1}$)
100
300
500
700
900
1100
1300
1500
1700
1900
2100
2300
2500
2700
2900
3100
3300

Figure 37B

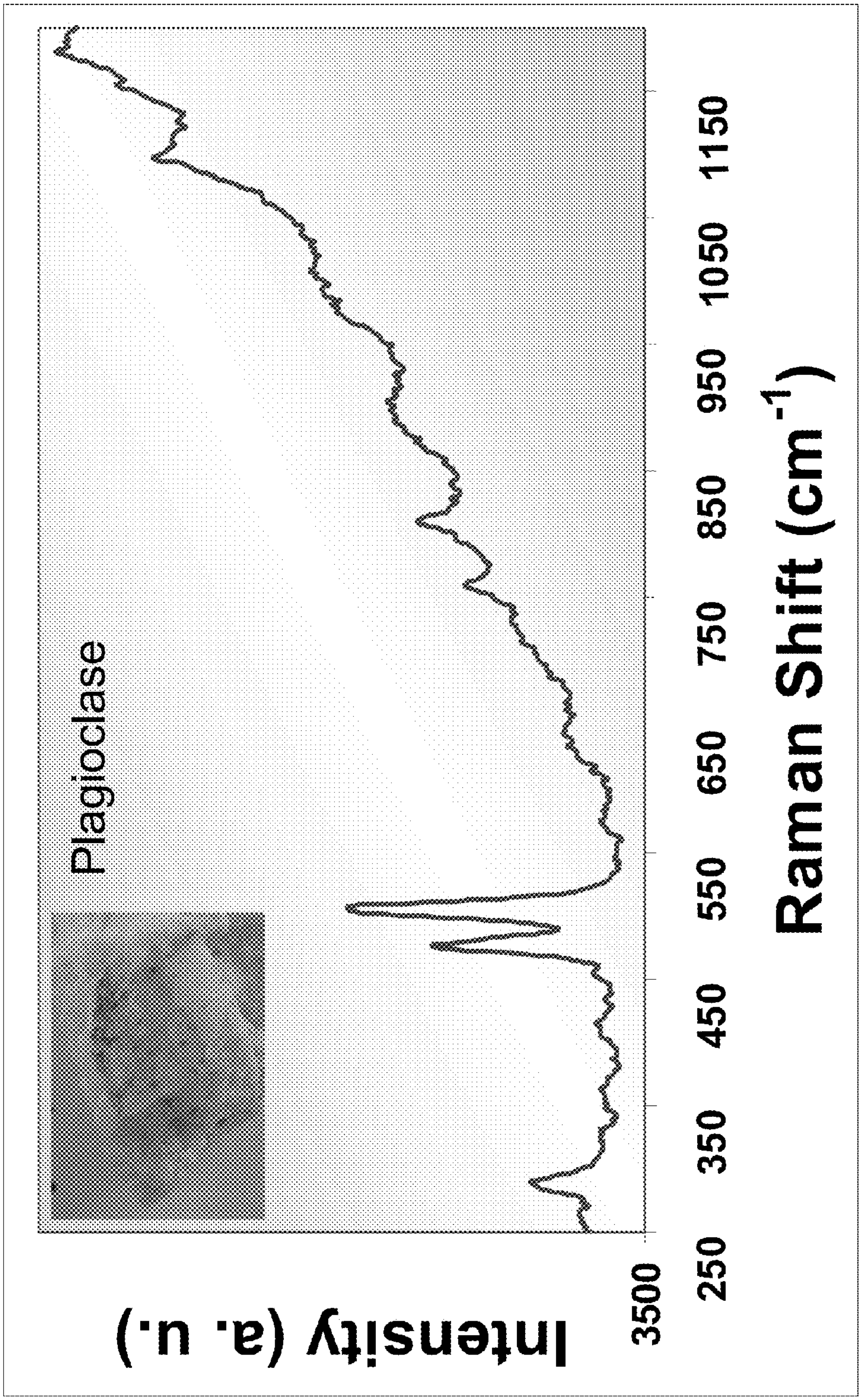

Plagioclase
Intensity (a. u.)
3500
250
350
450
550
650
750
850
950
1050
1150
Raman Shift (cm$^{-1}$)

Figure 37C

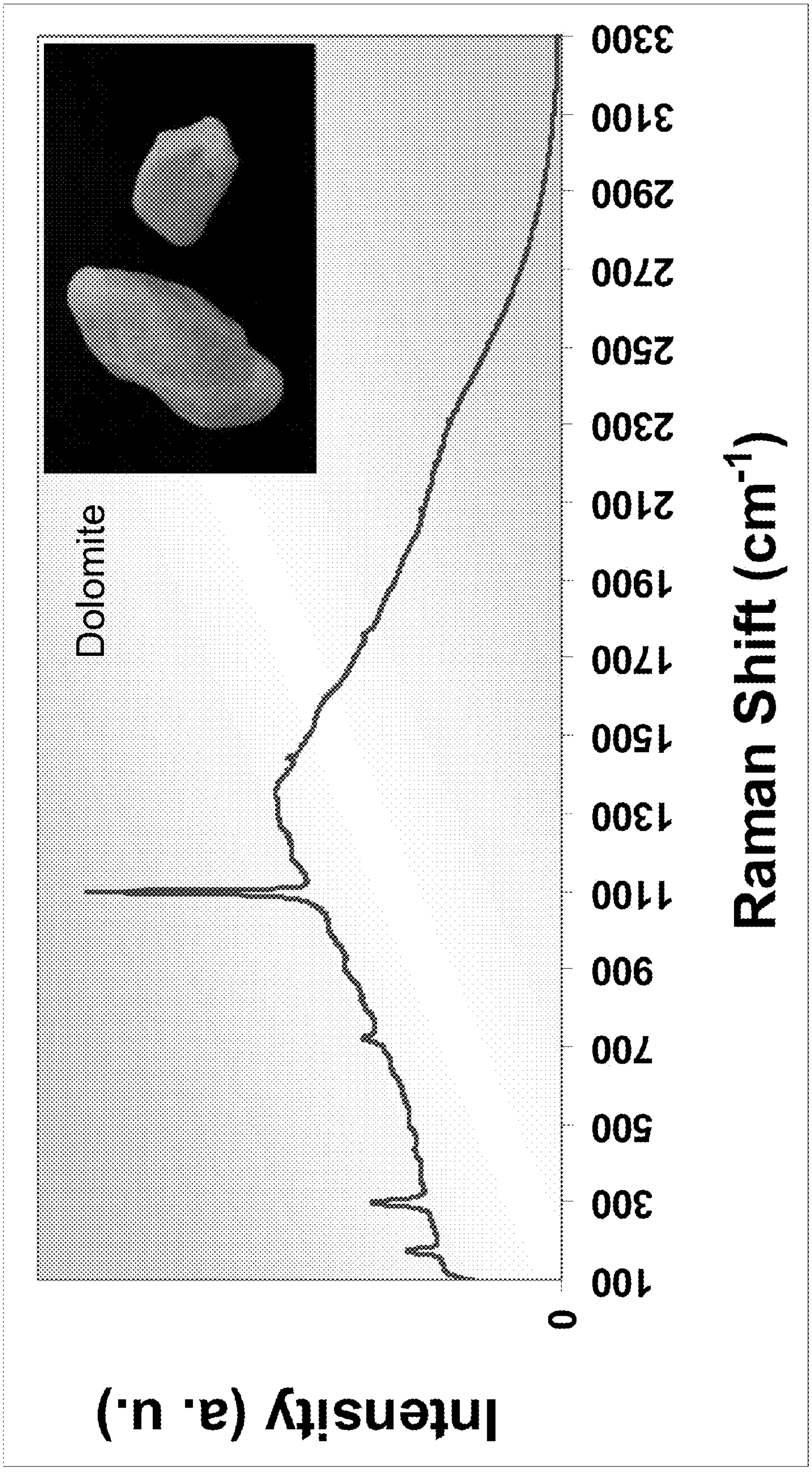

Dolomite
Raman Shift (cm$^{-1}$)
Intensity (a. u.)
0
100
300
500
700
900
1100
1300
1500
1700
1900
2100
2300
2500
2700
2900
3100
3300

Figure 37D

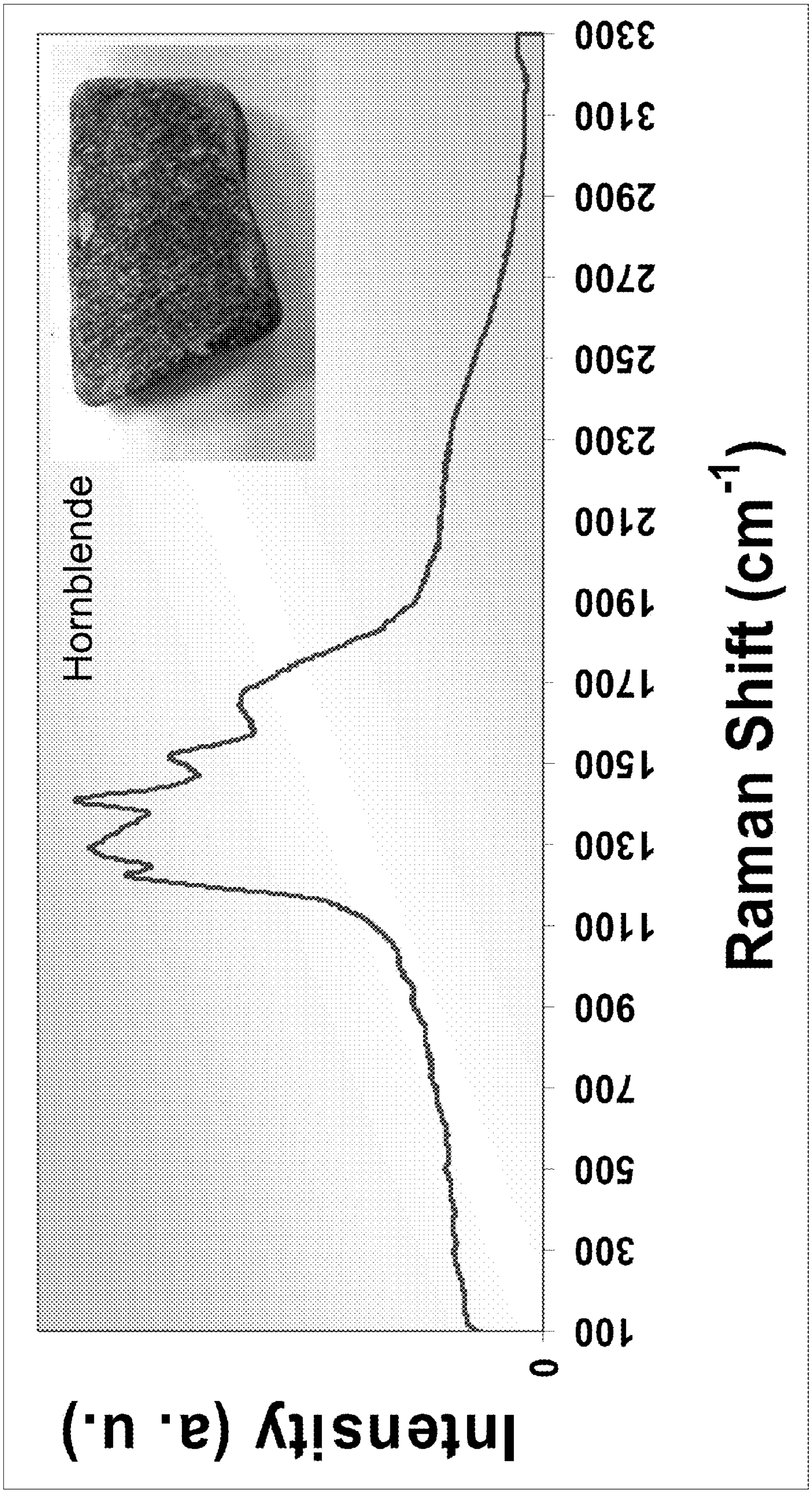

Hornblende
Intensity (a. u.)
0
100
300
500
700
900
1100
1300
1500
1700
1900
2100
2300
2500
2700
2900
3100
3300
Raman Shift (cm-1)

Figure 37E

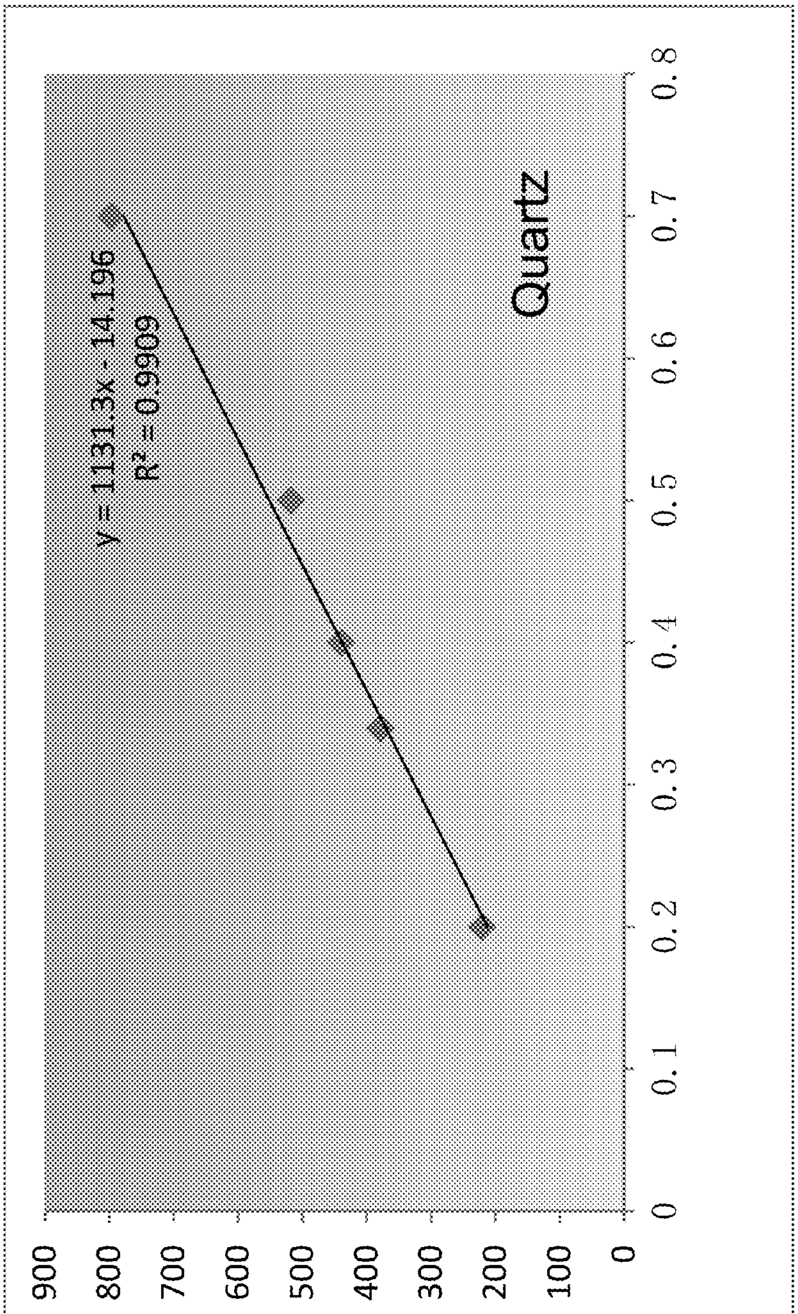

y = 1131.3x - 14.196
R² = 0.9909
Quartz
0
100
200
300
400
500
600
700
800
900
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8

Figure 38A

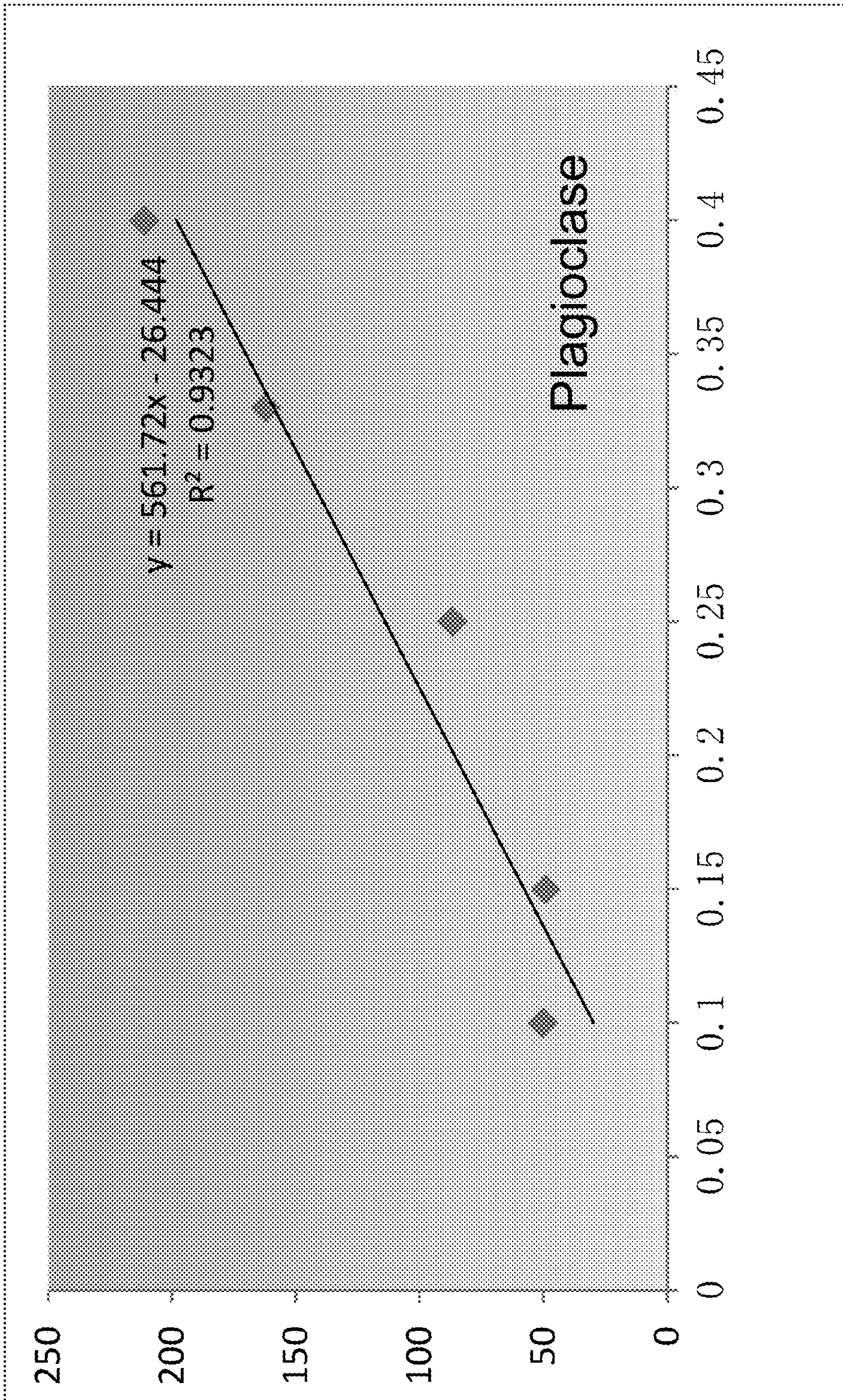

y = 561.72x - 26.444
R² = 0.9323
Plagioclase
250
200
150
100
50
0
0
0.05
0.1
0.15
0.2
0.25
0.3
0.35
0.4
0.45

Figure 38B

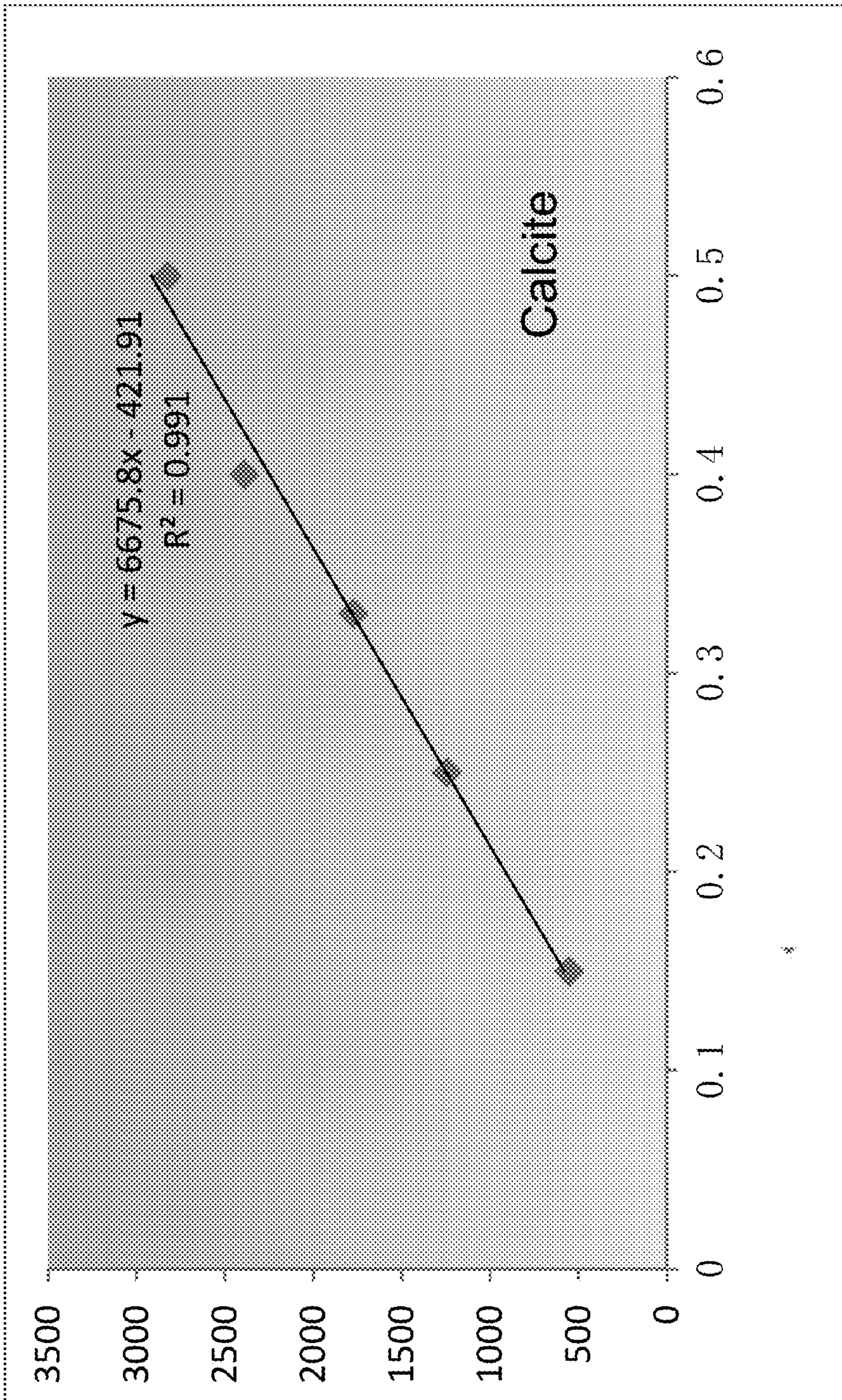

y = 6675.8x - 421.91
R² = 0.991
Calcite
3500
3000
2500
2000
1500
1000
500
0
0
0.1
0.2
0.3
0.4
0.5
0.6

Figure 38C

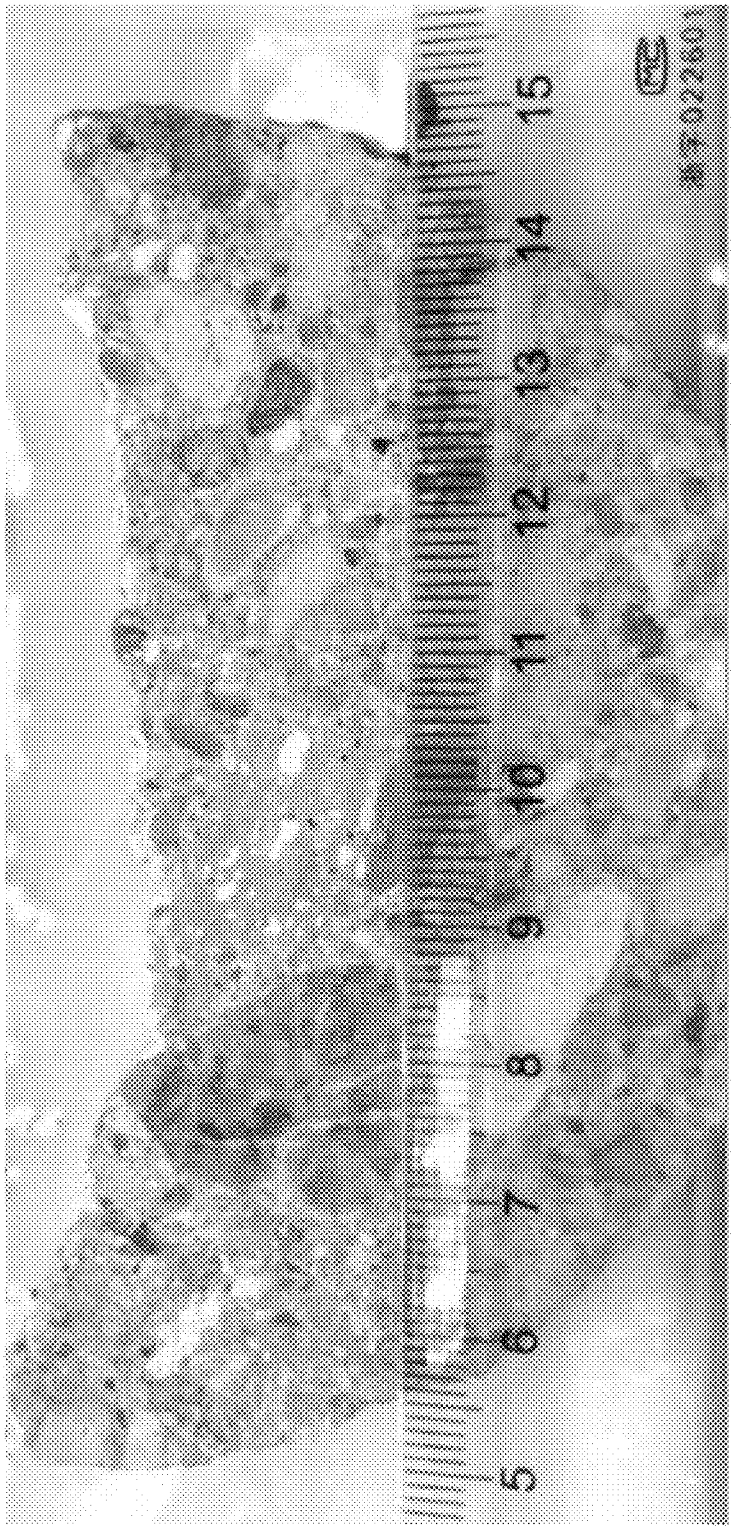



Figure 39

Mineral Mapping on a Rock Sample (upper surface) obtained using Raman Spectral Analysis

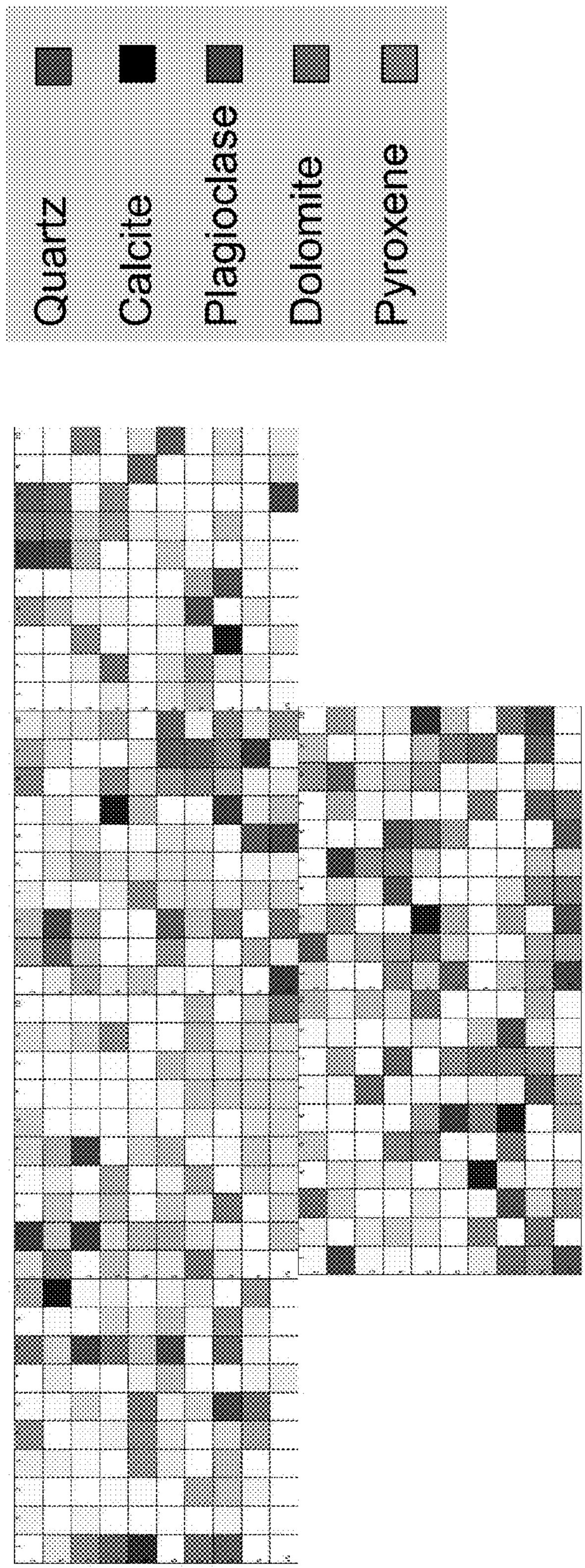



Figure 40A

Mineral Mapping on a Rock Sample (lower surface) obtained using Raman Spectral Analysis

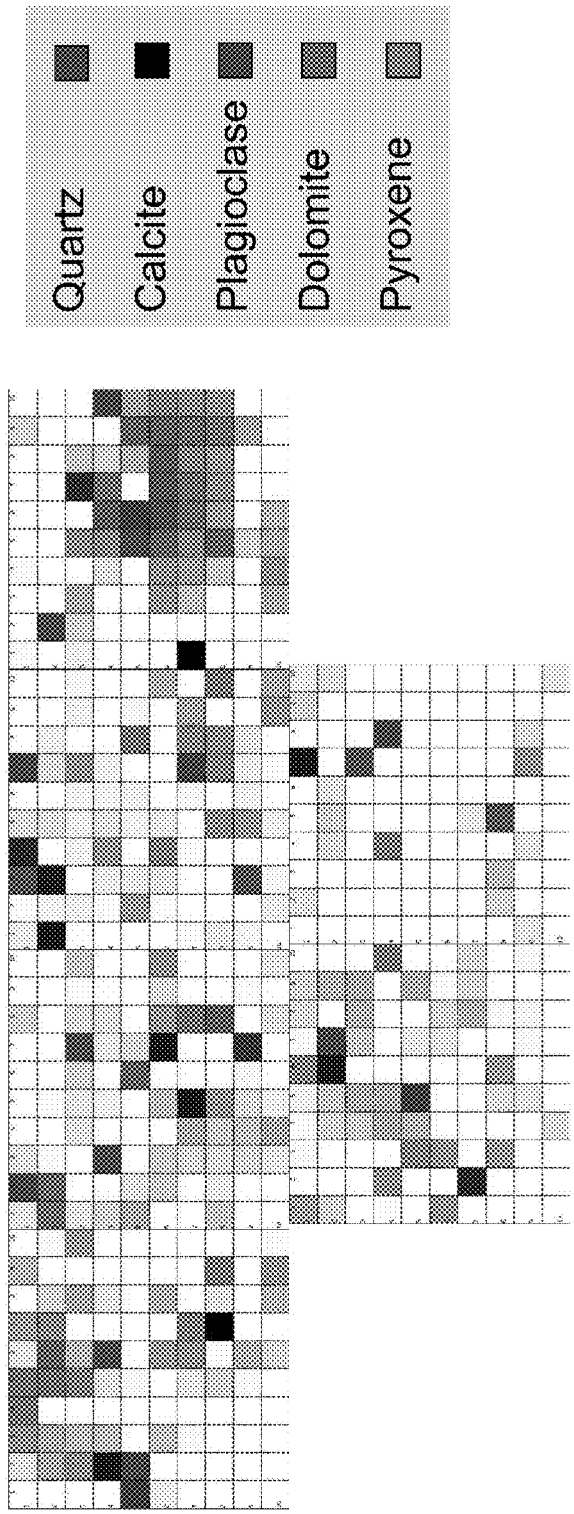



Figure 40B

Plagioclase Mapping on a Rock Sample obtained using Raman Spectral Analysis

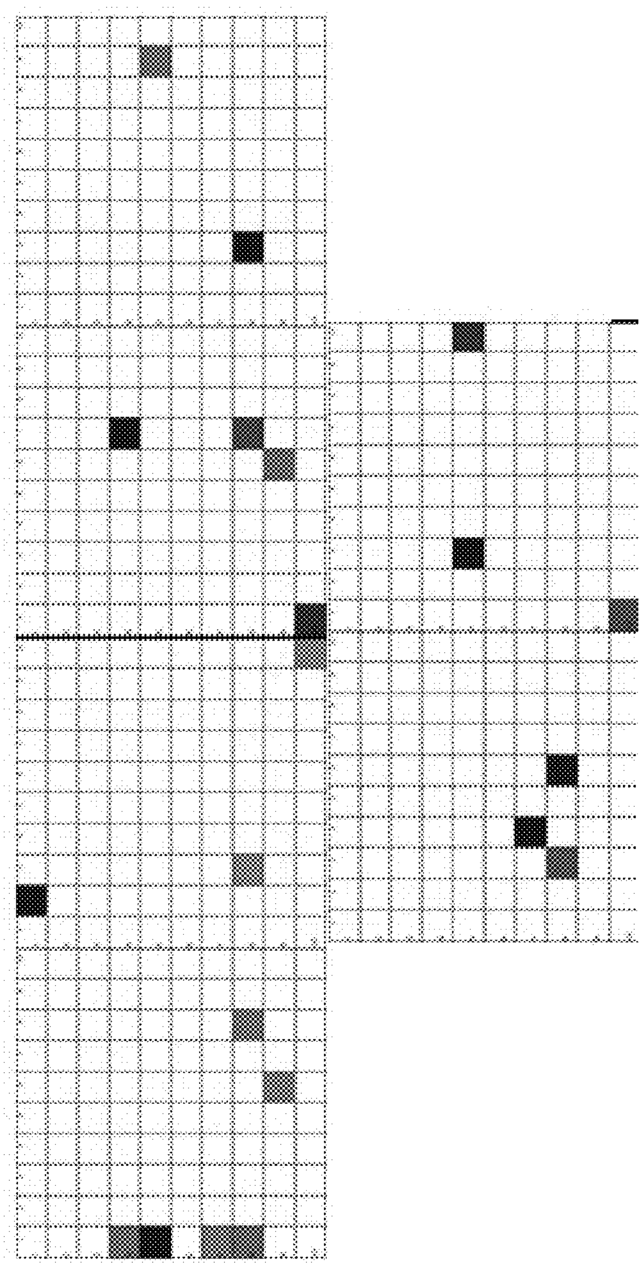


Figure 41

# SYSTEM AND METHOD FOR DETECTING OIL OR GAS UNDERGROUND USING LIGHT SCATTERING SPECTRAL ANALYSES

## FIELD OF INVENTION

This invention relates to technologies for detecting crude oil and gas from drilling mud or rock samples extracted from underground.

## BACKGROUND OF INVENTION

Raman scattering is an inelastic scattering of a photon which creates or annihilates an optical phonon. Raman scattering is the result of the interaction of incident photons with chemical molecular vibrations (i.e. phonons). A unique molecular structure results in a unique Raman scattering spectrum. Therefore, Raman scattering provides spectral fingerprint details about the molecules, and can also be used to distinguish molecular isomers and chiral molecules from each other.

Raman spectroscopy became commercially available after the invention of lasers in the late 1960's. A laser beam having a narrow line width is used to illuminate the testing chemicals in solid, liquid, or gas forms. The narrow line width of the laser beam can eliminate the overlaps of scattering peaks from photons with various wavelengths. The scattered light is collected by a photon detector such as Charge-Coupled Devices (CCD) or CMOS detector, which produces a Raman spectrum which is the intensity of the scattered light as a function of Raman shift defined as the wavenumber difference between the scattering light and incident laser. The spectral peaks in a Raman spectrum correspond to the vibration strengths of various molecular bonds, thus provide spectral fingerprints of the molecules.

Although Raman scattering is a useful analytical tool, Raman scattering has not been widely applied because of its weak scattering signals. Raman scattering has very weak signals due to the very small scattering cross section of molecules. Typically, only about $10^{-8}$ of the incident photons participates in Raman scattering. High power laser and high sensitivity CCD detector can be used to improve the scattering signals; however, it only makes limited improvement in detecting Raman scattered signal, and it requires extra costs and additional hardware, and can cause unexpected damages to samples.

Raman scattering signal can be enhanced by placing testing molecules in the vicinity of roughened surfaces. In Nano-Enhanced Raman Spectroscopy (NERS), or surface-enhanced Raman spectroscopy (SERS), a sample surface can be formed by deposition of metallic particles or clusters. The nano-enhanced Raman scattering phenomena can be explained by interaction between photons with localized electromagnetic field enhancement and chemical enhancement. The enhancement by SERS has been observed in different research labs. An Intel team used a porous silicon structure with coatings of noble metals such as silver on the surface, and demonstrated that Raman scattering signal increased as the porous silicon pore-size was decreased.

Accordingly, there is a need for low cost, convenient SERS devices for a wide-range of commercial applications.

## SUMMARY OF THE INVENTION

The present application discloses a convenient method for detecting oil and gas under the ground. The disclosed method is accurate and can be implemented in the field near the drilling hole where the drilling fluids and rock samples are collected. The disclosed methods can significantly shorten testing cycle times (from a day or days to minutes) and decreases measurement costs, compared to conventional testing methods.

Since nano-surface enhanced Raman spectral analysis is highly sensitive, the presently disclosed method is capable of detecting substances that are partially evaporated in the drilling samples (for example, mud, rock, etc.), during the drilling, or after the drilling sample is obtained but before the measurement. Thus, the presently disclosed method is especially advantageous for hydrocarbon molecules that have low boiling or vaporization temperatures, which are often rich in the content of oil or gas.

Another advantage of the presently disclosed methods is that the central office can instantaneously monitor testing results from multiple locations in the field, which allows the monitoring network system to have a global picture for potential oil and gas deposits in a large geological area.

Yet another advantage of the presently disclosed methods is that by providing testing in the field, feedback and guidance can be provided almost real time to the drilling strategies in the field. For example, if a drilling hole or rock core show promising oil/gas content at different depths underground, more drilling can be done at different depths or in the adjacent areas to explore detailed scope of the oil and gas deposits underground. If the in-field testing result is not promising at a location, the drilling team can quickly move on to the next location. Thus the entire drilling exploration is made more efficient by the presently disclosed methods.

In one aspect, the present invention relates to a method for detecting crude oil or gas in a drilling sample. The method includes introducing a drilling sample into a sample solution containing nano particles; illuminating the sample solution comprising the drilling sample and the nano particles by a laser beam; collecting light scattered by the drilling sample and the nano particles in the sample solution; obtaining a Raman spectrum from the light scattered by the drilling sample and the nano particles in the sample solution; identifying, in the Raman spectrum, a spectral signature associated with a substance around a predetermined Raman shift; and determining oil or gas content in the drilling sample based on the spectral signature of the substance in the Raman spectrum.

Implementations of the system may include one or more of the following. The drilling sample can be extracted from a first drilling hole in the ground, and wherein the steps of illuminating the sample solution and collecting light scattered by the drilling sample are conducted in the vicinity of the first drilling hole. The drilling sample can be collected in a first drilling hole underground, and the steps of illuminating the sample solution and collecting light can be conducted by a detector in the drilling hole underground. The method can further include adjusting drilling depths or locations of one or more drilling holes in real time in response to the crude oil or gas content determined in the drilling. The substance can include aromatic molecules. The substance can include at least one of a multi-ring aromatic molecule, thiophene, dibenzothiophene, methyl dibenzothiophene, phenanthrene, methylphenanthrene, carbazole, or a homologue of aforementioned molecules, n-hexane, cyclohexane, benzene, toluene, or xylene, otctane, heptane, or nonane. The substance can include nitrogen containing hydrocarbon compounds. The nitrogen containing hydrocarbon compounds can include carbazole or homologue compound molecules of carbazole. The substance can include sulfur containing hydrocarbon compounds. The sulfur containing hydrocarbon compounds can include dibenzothiophene or homologue compound molecules of dibenzothiophene. The spectral signature can include at least one spectral peak around the predetermined Raman shift. The method can further include determining a concentration of the substance in the drilling sample using the spectral signature. The method can further include after the step of introducing, allowing molecules in the drilling sample to adsorb to the nano particles in the sample solution. The sample solution can include multi-valence ions. The method can further include introducing an ionic material into the sample solution, wherein the sample solution has an ionic concentration in a range from about 10 μM to a saturation level. The nano particles can include a magnetic or ferromagnetic material. The method can further include applying an electrical field, a magnetic field, or an electro-magnetic field to the sample solution during the step of collecting. The nano particles can include a material selected from a group consisting of a metal, a metal alloy, an oxide material, silicon, a polymeric material, and a combination thereof. The nano particles have an average dimension in a range from about 1 nm to about 10 μm. The nano particles can have an average dimension in a range from about 5 nm to about 500 nm. The nano particles can have a size distribution characterized by an average dimension and a width, wherein the ratio of the width to the average dimension is in a range from about 0.01 to about 3. The nano particles can include carbon nano tubes.

In another aspect, the present invention relates to a method for predicting presence of crude oil or gas in the underground. The method includes defining an array of sample dots on a surface of a sliced rock sample obtained from underground; illuminating each of the sample dots on the surface of the sliced rock sample by a laser beam; collecting light scattered by the surface of the sliced rock sample at each of the sample dots; obtaining a Raman spectrum from the surface of the sliced rock sample at each of sample dots; determining a mineral content at each of the sample dots on the surface of the sliced rock sample based on the Raman spectrum; obtaining a map of mineral content on the surface of the sliced rock sample; and predicting a probability of crude oil or gas underground using the map of mineral content.

Implementations of the system may include one or more of the following. The method can further include establishing Raman spectral signatures in a plurality of minerals, wherein the step of determining a mineral content includes identifying a Raman spectral signature associated with one of the plurality of minerals in the Raman spectrum. The method can further include for at least one of the plurality of minerals, establishing a quantitative dependence of spectral intensity at one of the Raman spectral signatures as a function of the concentration of the one of the plurality of minerals, wherein the step of determining a mineral content includes calculating a concentration of the one of the plurality of minerals based on the function and spectral intensities at the spectral signature. The sliced rock sample can be extracted from a first drilling hole in the ground, and wherein the steps of illuminating and collecting light are conducted in the vicinity of the first drilling hole. The method can further include in response to the map of mineral content on the surface of the sliced rock sample, adjusting drilling depths or locations of one or more drilling holes in real time. The mineral content includes one or more of Quartz, Calcite, Plagioclase, Dolomite, Pyroxene, Chlorite, Kalifeldspar, Na-feldspar, Amphibole, MuscLaumontite and analcime ovite, Biotite, Ankerite, Siderite, Anhydrite, Gypsum, Thenardite, Barite, Pyrite, Glauberite, Laumontite, Analcime, Illite, Smectite, Kaolinite, Corundum, Ankerite, Halite, Mica, Hornblende, or Granite.

In another aspect, the present invention relates to a method for predicting presence of crude oil or gas in the underground. The method includes receiving a drilling sample to detect hydrocarbon gases extracting from a drilling sample, which include, but not limited to, $CH_4$, $C_2H_6$, $iC_4H_{10}$, $nC_4H_{10}$, $iC_5H_{12}$, $nC_5H_{12}$, $C_mH_n$ (m is an integer, 1, 2, 3, etc., n=2×m+2). It is also valuable to be able to detect non-hydrocarbon gases, including $O_2$, $N_2$, CO, $CO_2$, $H_2$, $H_2S$, $SO_2$, $NH_3$, etc. using a Raman sensor.

In another aspect, the present invention relates to a method for predicting presence of oil or gas in the underground. The method includes receiving a drilling sample and a sliced rock sample obtained from a same geological location; introducing the drilling sample into a sample solution containing nano particles; illuminating the sample solution comprising the drilling sample and the nano particles by a first laser beam; collecting light scattered by the drilling sample and the nano particles in the sample solution; obtaining a first Raman spectrum from the light scattered by the drilling sample and the nano particles in the sample solution; identifying, in the first Raman spectrum, a spectral signature associated with a substance around a predetermined Raman shift; determining oil or gas content in the drilling sample based on the spectral signature of the substance in the first Raman spectrum; illuminating a surface of the sliced rock sample by a second laser beam; collecting light scattered by the surface of the sliced rock sample at each of the sample dots; obtaining a second Raman spectrum using the light scattered from the surface of the sliced rock sample at each of sample dots; determining a mineral content at each of the sample dots on the surface of the sliced rock sample based on the second Raman spectrum; and predicting a probability of crude oil or gas underground using the mineral content and crude oil or gas content in the drilling sample.

These and other aspects, their implementations and other features are described in detail in the drawings, the description and the claims.

## BRIEF DESCRIPTION OF THE DRAWINGS

FIG. **1** is a top view of a square array of an array device according to the present invention.

FIGS. **2**A and **2**B show a square array according to the present invention.

FIGS. **3**A and **3**B show a square array according to the present invention.

FIG. **4** is a top view of another square array according to the present invention.

FIGS. **5**A and **5**B show a square array with isolated active areas and surrounding inactive areas.

FIGS. **6**A and **6**B show a square array with a layer of active material connecting each of the active nano surface structure.

FIG. **7** is a three dimensional view of cylindrical form of array of independent active nano surface structures on surrounding inactive area, with an inactive area depression at the bottom of each of the active nano surface structures.

FIGS. **8**A and **8**B are top views of circular arrays.

FIGS. **9**A-**9**E show top views of arrays of various shapes.

FIG. **10** shows an array comprising sub-arrays with various shapes.

FIG. **11** shows an array comprising sub-arrays with various sizes.

FIG. **12** is a cross sectional view of an array with a surface adsorption layer over the entire array.

FIG. **13** is a cross sectional view of an array with a surface adsorption layer selectively covering active SERS nano surfaces.

FIG. **14** is a cross sectional view of an array with a surface adsorption layer selectively covering active SERS nano surfaces according to the present invention.

FIG. **15** is a cross sectional view of an array with a surface adsorption layer selectively covering inactive SERS nano surfaces.

FIG. **16** is a cross sectional view of an array device with a function layer between a substrate and an array of nano structures.

FIG. **17** shows another array device with a function layer.

FIG. **18** is a flow chart of a method in accordance with the present invention.

FIGS. **19**A-**19**D show a process for forming an array device in accordance with the present invention.

FIGS. **20**A-**20**E show another process for forming an array device in accordance with the present invention.

FIGS. **21**A-**21**D show yet another process for forming an array device in accordance with the present invention.

FIG. **22** is a diagram of a SERS system using an array device in accordance with the present invention.

FIGS. **23**A and **23**B are schematic diagrams respectively showing the physical mechanism of Raman scattering and a Raman experiment setup. FIG. **23**C also shows exemplified Raman spectra obtained from different chemicals.

FIG. **24** shows scanning-electron micrographs (SEM) obtained from the top-view of a surface structure, where d is the average diameter of nano holes, and D is the averaged center-to-center distance between adjacent nano holes.

FIG. **25** shows a normal Raman spectrum and SERS spectra of methamidophos.

FIG. **26** is a block diagram of an exemplified monitoring network system in accordance to the present invention.

FIG. **27** shows the details of an exemplified mobile detector in accordance to the present invention.

FIG. **28** illustrates an exemplified process for the operations of the monitoring network system.

FIG. **29** is a block diagram of another exemplified monitoring network system in accordance to the present invention.

FIG. **30** illustrates an exemplified process for determining potential oil content in drilling fluid.

FIG. **31** is a schematic diagram showing a configuration for detecting chemical substance in a drilling sample using a test reagent or a nano chip containing nano particles and a light scattering probe.

FIG. **32** show exemplified micrographs of the nano particles shown in FIG. **31** using scanning electron microscope.

FIG. **33** illustrates an exemplified size distribution of the nano particles in the sample solution shown in FIG. **31**.

FIG. **34** illustrates exemplified nano-enhanced Raman spectra obtained from drilling mud samples extracted at different depths of a drilling hole.

FIGS. **35**A-**35**C illustrate Raman spectral signatures for methyl dibenzothiophenes (MDBTs) at different concentrations which are used to identify MDBTs in drilling mud samples.

FIG. **36** illustrates an exemplified process for detecting mineral compositions in rock samples to determine probability of crude oil or gas underground.

FIGS. **37**A-**37**E illustrate Raman spectra and spectral signatures of several common minerals in rock samples.

FIGS. **38**A-**38**C illustrate Raman spectral intensities at the spectral signatures as a function of concentration for several common minerals in rock samples.

FIG. **39** shows an example of a sliced rock sample.

FIGS. **40**A and **40**B respectively show Raman mapping (or sampling dot arrays) on the two surfaces of the sliced rock sample in FIG. **39** and results of Raman spectral analyses at the sampling dots.

FIG. **41** shows Raman mapping of plagioclase and its concentration across an array of sampling dots on the top surface of the sliced rock sample in FIG. **39**.

## DETAILED DESCRIPTION OF THE INVENTION

The present invention provides new devices and apparatus/systems as well as methods for improved performance of Nano-Enhanced Raman Spectroscopy (NERS), or called Surface-Enhanced Raman Spectroscopy (SERS).

SERS selectivity of surface signal results from the presence of surface enhancement mechanisms demonstrated only at the surface of nano particles. There are two primary mechanisms of surface enhancement: electromagnetic enhancement and chemical enhancement. The electromagnetic enhancement is dependent on rough features, nano particle size, shape and distribution present on a surface with nano particles, while the chemical enhancement involves electronic charge transfer and changes to the adsorbate electronic states due to chemisorption of the analytes.

SERS is observed primarily from analytes adsorbed onto coinage (Au, Ag, and Cu) or alkali (Li, Na, K) metal surfaces, with the excitation wavelength near or in the visible region. Theoretically, any metal would be capable of exhibiting the effect of surface enhancement, but the coinage and alkali metals satisfy calculable requirements and provide the strong enhancement.

The great part of the overall enhancement of SERS is due to an electromagnetic enhancement mechanism that is a direct consequence of the presence of metal roughness features, nano particle size, shape and distribution present on a surface with nano particles, or nano particle size, shape and distribution present in a test reagent containing nano particles.

The chemical enhancement mechanism also provides enhancement for the gain of Raman signal intensity. The molecule is adsorbed onto the surface and interacts with the surface. The chemical enhancement exists because of this interaction. The metal adsorbate proximity allows pathways of electronic coupling from which novel charge-transfer intermediates emerge, leading to a SERS condition with higher Raman scattering cross-sections. In addition, the electronic orbits of the adsorbate molecules may contact and interact with the conducting electrons of the metal, altering the chemical state of the chemical substance. It is also proposed that the chemical enhancement may be an alteration in the scattering cross-section, which is the chemical nature of the chemical substance changing due to its interaction with the metal.

The present invention provides an array device comprising a substrate, or the nano particles in a test reagent, supporting a plurality of nano structures and an exposed sensing surface upon the nano structures, wherein said surface includes at least one active SERS nano surface and at least one inactive SERS nano surface established in proximity to the active SERS nano surface. Accordingly, the performance of this SERS device benefits from both electromagnetic effect and chemical enhancement to the Raman signal intensity.

The term, "active SERS nano surface", when used herein, encompasses a well-defined metal surface having at least one surface dimension on a nanometer scale. The surface may or may not be flat. The active SERS nano surface exhibits electromagnetic enhancement to Raman signal under photon irradiation. Examples of materials for the active SERS surface include noble metal such as Ag, Au, Cu, and Pt, and transition metals such as Al, Fe, Co, Ni, Ru, Rh, and Pd. The material used for the active SERS surface is referred as "active material".

The term, "inactive SERS nano surface", refers to a surface having at least one dimension on a nanometer scale. The surface may or may not be flat. In contrary to the active SERS nano surface, the inactive SERS nano surface does not exhibit significant electromagnetic enhancement to Raman signal just by itself. However, when the inactive SERS surface was placed in proximity to the active SERS nano surface, a relatively stronger enhancement of Raman signal was observed, compared with the signal from merely the active SERS nano surface. Therefore, the inactive SERS nano surface arranged in an alternative fashion with the active SERS surface provides further enhancement to Raman signal. Examples of materials for the inactive SERS nano surface include insulators such as $SiO_2$, $Al_2O_3$, $Si_3N_4$, $Ta_2O_5$, $TiO_2$, and air (open space). The material used for the inactive SERS nano surface is referred as "inactive material".

The term, "nano structure", as used herein, is intended to mean a 3-dimensional object either extruded away from the substrate or recessed toward the substrate, or small size particles having at least one dimension on a nanometer scale, or the nano particles in a test reagent. Non-limiting examples of the shape of the nano structure include nano rod, nano pyramid, nano hole, nano pit, and nano particles at the surface of a substrate, or nano particles in a solution, or a test reagent, containing noble metal (such as silver Ag, gold Au, etc.) nano particles with averaged particle size in the range of about 2 and about 100 nm, Then, light scattered by the mixed sample solution, with or without the nano-scale surface structure, and the adsorbed molecules is collected.

According to one embodiment of the present invention, an improved SERS performance is achieved by arranging the inactive SERS nano surface next to the nano active SERS surface. FIGS. **1-11** provide exemplary array devices for improved SERS applications.

FIG. **1** is a top view of a square array **100** with a plurality of active SERS nano surfaces **110** and inactive SERS nano surfaces **120** established on a substrate, or the nano particles in a test reagent. As shown in FIG. **1**, each active SERS nano surface is alternatively arranged with each inactive nano SERS surface. The active SERS surfaces are made from a material selected from a group of noble metals, including but not limited to Ag, Au, Cu and Pt. The active SERS surfaces may also be made from a material selected from a group of transition metals, including but not limited to Al, Fe, Co, Ni, Ru, Rh, and Pd. The inactive SERS nano surfaces are made from insulating materials, including but not limited to $SiO_2$, $Al_2O_3$, $Si_3N_4$, $Ta_2O_5$, $TiO_2$, and open space (air).

FIG. **2**A shows a perspective view of an array device **200** according to one aspect of the present invention. The device comprises a substrate **210**, an array of rectangular rods **220** made of an active material and an array of rectangular rods **230** made of an inactive material. Each active rod **220** is alternatively arranged with each inactive rod **230**. The active rod **220** provides the active SERS nano surface **225** and the inactive rod **230** provides the inactive nano SERS **235**. Both surfaces **225** and **235** are substantially square, having dimensions of **226**, **227**, **236**, and **237** between about 5 nm to 300 nm. In one embodiment, the dimension of the squares is between about 1 nm and about 10 μm.

FIG. **2**B is a sectional view of the structure of FIG. **2**A, sliced at line X-X' of the structure shown in FIG. **1**. The height **228** of the active surface **225** is substantially equal to the height **238** of the inactive surface **235**. The height **228** and **238** is between 5 nm to 1000 nm. In one embodiment, the height **228** and **238** is between 1 nm to 5 μm.

FIG. **3**A shows a perspective view of another square array **300**. The substrate **310** is made from an inactive material. A plurality of square rods **320** are formed on the substrate. The rod **320** provides the active SERS nano surface **330**, which includes top surface **335** and side wall **336**. The active SERS nano surface **330** is surrounded by four square areas **340** of inactive SERS nano surfaces. The square area **335** of the active SERS surface is substantially equal to the inactive area **340**. A sectional view of a cutoff at line X-X' is shown in FIG. **3**B. The height **350** of the rod **320** is between 5 nm to 1000 nm. In one embodiment, the height **350** of the rod **320** is between 1 nm to 5 μm.

The detection sensitivity of the Raman scattering sensors can be enhanced when at least a portion of the nano structures or nano surfaces (active or inactive) has a nano feature size functionally matched with a characteristic parameter of electrons or phonons such as an electron mean-free path (MFP) of electrons on the surface, electron wavelength of electrons on the surface, a phonon MFP of phonons on the surface and a phonon wavelength of phonons on the surface.

The term "nano feature size" is used herein to refer to the dimensions of an active nano SERS surface such as the diameter of an active nano SERS surface, the height or depth of a nano rod or a nano hole, or the spacing between nano structures in the array device.

The term, "functionally match" as described above may include the condition that the nano feature size is approximately equal to, smaller than, integer numbers of, or with a special mathematical function to the characteristic parameter of electrons or phonons.

FIG. **4** shows another example of a square array **400** of nano surface structure where the active SERS surfaces **410** are physically isolated from each other by inactive SERS nano surface **420**. Again, the spacing between the active areas can be air or insulating materials as illustrated in FIGS. **2** and **3**.

Referring now to FIGS. **5**A and **5**B, an array device **500** having square rods **520** of an active material is established on a substrate **510**. Each rod **520** is surrounded by a region **530** made of an inactive material. A cutoff view from line X-X' is shown in FIG. **5**B. Each active SERS nano surface **525** is isolated by an inactive nano surface **535**.

In some embodiments, FIG. **6**A is a perspective view showing an array device **600** having a substrate **610** covered by a layer **630** of an active material. Square rods **620** of another active material established on the layer **630**. A cutoff view from line X-X' is shown in FIG. **6**B. Each active SERS nano surface **625** is isolated by another active nano surface **635**. In a special case, a same active material is used for both square rods **620** and layer **630** and the active structures are connected at the bottom of the active areas. The connecting materials can be same as in the active area or different conductors.

It is to be understood that the shapes of the nano structures can be altered as desired for specific applications. FIGS. **7-9**E show examples of nano rods or nano holes. FIG. **7** shows a perspective view of cylindrical form of array of nano surface structures **700**. The independent active areas in their cylindrical forms **710** are regularly distributed on surrounding inactive area **720** to form an array of the nano surface structures **700**. The bottom of each of the active cylinder is situated on a depression **725** in the inactive area **720**. The depth **730** of the depression in the inactive area is smaller than the height **750** of the cylindrical active rod **710**. The diameter **740** of the depression **725** is larger than the diameter **760** of the active rod by a distance on a nanometer scale. Various geometrical features can be designated to maximize the adsorption of molecules. The depression shown on this figure is one of the examples of the enhancement providing structure.

FIG. **8**A shows a top view of circular array **800** of nano surface structures which are regularly distributed on a substrate. The area in circles **810** can be the active SERS nano surface or the inactive SERS nano surface (or even air, meaning empty). FIG. **8**B shows a top view of another circular array **850** of nano surface structure with a tight packaging of the circles on a substrate.

FIG. **9**A shows a top view of an array **900** of rectangular nano surface structures **905**. FIGS. **9**B-**9**E show a top view of arrays **910**, **920**, **930**, and **940** of triangular **915**, round rectangular **925**, diamond **935**, and oval **945** shapes of nano rods or nano holes.

FIGS. **10** and **11** illustrate that an array device can include a number of sub arrays on a substrate. An advantage of the combination of the sub-arrays is that the nano surface structures are optimized for chemical measurement by SERS for a wide range of substances. The combination of different arrays can be used as a general Raman enhancement tool.

FIG. **10** shows a top view of an array device **1000** having sub-arrays **1010**, **1020**, **1030**, and **1040**. Each of the sub-arrays has different shapes of the nano structures. FIG. **11** illustrate an array device **1100** having sub-arrays **1110** and **1120**. The sub-arrays may have the same shape but have different size.

With reference now to FIG. **12**, an array device **1200** which has an adsorption layer **1210** over a structure **1220** which is similar to array **200** or **500** shown in FIG. **2** and FIG. **5** respectively. Based on the specific chemical bonding configurations of a measured chemical in SERS, the surface adsorption layer **1210** can be selected with adequate chemical bonds, either positive charged or negative charged, so that the measured chemicals can be adsorbed to the surface, and moved to close to and then adsorbed onto the active areas. The adsorption layer does not need to be very thick. In some cases, a monolayer or even island distributed layer will be sufficient. The layer thickness can be between 0.5 nm and 500 nm, preferred between 2 nm-20 nm. Materials suitable for the adsorption layer include Ag oxide, Au mixed with oxide, $TiO_2$, $SiO_2$, $Al_2O_3$, $Si_3N_4$, $Ta_2O_5$, ZnO, Zr oxide, Hf oxide, Y oxide, Ag oxide, Au oxide, Sn oxide, Sb oxide, or other metal oxide layer, metal layer doped with chlorine or chloride, polymers, etc.

FIGS. **13**-**15** illustrate various arrangements of the adsorption layer over an array device. In one embodiment, the adhesion layer covers only the active SERS nano surfaces. FIG. **13** shows an array device **1300** having the adsorption layer **1310** disposed selectively on the inactive SERS nano surfaces **1325**. The structure **1320** is similar to the array device **200** or **500** shown in FIGS. **2** and **5** respectively. Alternatively, an adsorption layer **1410** may be selectively disposed on the active SERS nano surface **1420** for array **1400** shown in FIG. **14**.

In another embodiment, an adsorption layer **1510** may be selectively disposed on top portion of the isolated inactive SERS nano surface **1520** as shown in FIG. **15**. The structure **1530** is similar to the array structure **300** shown in FIG. **3**.

The presently disclosed device is compatible with other arrangements of the adsorption layer, which can help bring molecules of an analysis close enough to the active nano SERS surface.

In some embodiments, an enhancement of molecule adsorption to the device surface is provided by electrical biasing. FIG. **16** shows a device **1600** of an array of nano surface structure **1640** with active and inactive SERS nano surfaces **1650** and **1655** over a metallic layer **1620** on a substrate **1610**. There is an optional insulator layer **1630** separating the array **1640** from the metallic layer **1620**. Based on the charge states of the measured chemical molecules, a positive or negative bias can be applied to the metallic layer **1620** to attract the molecules to the sensing surface **1650** and **1655**.

The metallic layer **1620** is also referred as a function layer. The term, "function layer", as used herein, refers to a layer providing electrical, magnetic, or thermal bias to the array device of nano surface structure.

In some embodiments, molecular adsorption to the device surface can be enhanced by lowering the temperate of the whole array. Given that the array is much thinner than the substrate, a thermal electrical cooler can be connected to the bottom of the substrate, or to the metal pad area of a sensing chip. Referring to FIG. **17**, an array device **1760** includes a thermally conductive substrate **1780**. By applying an electrical field to a cooler, the substrate **1780** including the nano array **1770** can be cooled down to, for example, a temperate range from −20° C. to 20° C. A lower temperature can be achieved by using a more expensive thermal electrical or other cooler. The lower the surface temperature, the more molecules will be condensed on the surface. By targeting cooled temperature to a sensing chip, selected chemical molecules depending on their boiling temperature would be adsorbed onto the surface.

In some embodiments, the function layer can be used for the purpose of applying a proper DC or AC biasing voltage to the device to attract chemical molecules since many of interested molecules carry positive or negative electric charges. Furthermore, the function layer provides a means to heat the sensing surface to vaporize unexpected/unwanted surface contamination and/or burn out surface contamination. The materials of the conductive layer can include, but not limited to, Ti, Ni, Cr, Pt, Ru, Ni—Cr alloy, NiCrN, Pt—Rh alloy, Cu—Au—Co alloy, Ir—Rh alloy or/and W—Re alloy. The conductive layer can have both good electrical and thermal conductivity, good adhesion to both silicon substrate and metallic sensing surface layer.

In some embodiments, the magnetic field is supplied by the function layer to the sensing chip, or by an external source. In this way, the chemical polar molecules on the sensing surface would have statistically preferred orientation; on the other hand, the chemical polar molecules under test could have their statistically preferred orientation. The effect of applied magnetic field or built-in magnetic materials at function layer is to enhance chemical specific binding, i.e., enhancing chemical molecule adsorption onto the sensing surface, so that to enhance Raman signal. The applied magnetic field can be parallel or perpendicular to the sensing surface. The magnetic field strength is ranging from 0.5 to 3000 gauss, or 2 to 100 gauss.

FIGS. **18**-**21** illustrate a number of examples of the array device. It will be appreciated that the described processes need not to be performed in the order in which they are herein described, but that these descriptions are merely exemplary of preferred methods making the array device. In addition, it is understood and appreciated that the scale of the components and features illustrated in the figures has been exaggerated to facilitate ease of discussion.

FIG. **18** is a flowchart of a method of forming the array device. As indicated in block **1810**, the process is commenced by providing a substrate. In at least one embodiment the substrate is a Si wafer. An inactive material may also be used as the substrate. At least one layer of material is deposited upon the substrate, block **1820**. A pattern is then established upon the layer of material, block **1830**. The pattern provides areas defining a plurality of nano structures. As in block **1840**, a portion of the layer of material are removed, so that side walls of the nano structures are formed. The method further includes forming an exposed sensing surface upon the nano structures, wherein said surface comprises at least one active SERS nano surface and at least one inactive SERS nano surface established in proximity to the active nano SERS surface.

FIGS. **19**A-**19**D provide detailed illustrations for making the nano structures in a sensor array in according to the present invention. The substrate **1900** is made from an inactive material. Alternatively, the substrate can be a non-inactive material with a coating of a layer of an inactive material to provide the inactive SERS nano surface for the completed device.

As shown in FIG. **19**A, an optional adhesion layer **1910** is deposited upon the substrate to adhere nano structures onto the substrate. Non-limiting examples of materials for the adhesion layer are Ti and Ni. The thickness of the adhesion layer can be between 10 to 100 nm.

Upon the adhesion layer, a layer of active material **1920** is deposited thereon. The thickness of the active layer **1920** is between 1 nm to 5 μm. In an embodiment, the thickness of the active layer **1920** is between 5 nm to 100 nm. A mask layer **1930** is then deposited on the layer of active material **1920**. An example of the mask layer is a layer of photoresist or e-beam resist. An optional metal layer may be established between the resist layer **1930** and active layer **1920** to serve as a hard mask in subsequent processes.

Next, a pattern on the resist layer **1930** is established by a photolithography process or e-beam process (FIG. **19**B). Photolithography and e-beam patterning techniques are well known to those skilled in the art and commercially available and need not be described in more detail herein.

Next, the exposed portion of the active material and the adhesion layer are removed by etching processes such as wet chemical etching or plasma etching (FIG. **19**C). The inactive SERS nano surfaces **1940** are formed around nano rods **1955**. The remaining mask layer **1930** is finally removed. As shown in FIG. **19**D, the completed device has a plurality of nano rods with the active SERS nano surfaces **1950** formed on the top and side wall surfaces of the rods. These active surfaces are surrounded by the exposed inactive SERS nano surface **1940**.

In an alternative embodiment, layer **1900** can be an active material and layer **1920** can be an inactive material. The above detailed process can produce a device with an array of nano rods of the inactive material, in which the inactive SERS nano surfaces are surrounded by the active nano SERS surface.

A sequence of steps of yet another embodiment of forming array device is shown in FIGS. **20**A-**20**E. A pattern of the nano structures is defined by an imprint lithography process. The pattern can be produced on a substrate such as a silicon wafer by e-beam lithography and reactive ion etching. The patterned substrate can act as a mold. The pattern in the nano scale is a reverse image of a final nano array. In the first step, a layer of inactive material **2010** may be deposit onto the substrate **2000** to establish the inactive nano SERS surface. A layer of active material **2020** such as Ag or Au is then deposited onto the inactive layer. Then a layer of imprintable material **2030**, such as a PMMA or other polymer, is coated on layer **2020**. The mold **2040** is then pressed into layer **2030** (FIG. **20**A). Imprinting is made during the step after removing the mold (FIG. **20**B). In FIG. **20**C, pattern transfer is complete using etching to remove residual resist **2035** in the compressed areas. Further chemical etch can be used to etch the metal film in the compressed areas (FIG. **20**D). An array of nano surface structure is produced after removing the mask layer. As shown in FIG. **20**E, the completed device has a plurality of nano rods with the active SERS nano surfaces **2050** formed on the top and side wall surfaces of the rods. These active surfaces are surrounded by the exposed inactive SERS nano surface **2040**.

In some embodiments, FIGS. **21**A-**21**D show an array of nano structure formed by anodization process. FIG. **21**A shows a stack of layers deposited on a substrate **2100**. The substrate **2100** may be a silicon wafer. The first layer **2110** is an inactive material. This layer can be 30-50 nm $SiO_2$ made by oxidizing silicon wafers. Above the inactive layer, an adhesion layer **2120** is deposited. The thickness of the adhesion layer is usually controlled in the range of 100 Å-1,000 Å and optimized to provide best adhesion to a noble metal layer, e.g., an Ag or Au layer. The thickness of the adhesion layer **2120** is also optimized for applying an electric bias to the sensing surface for trace chemical detection and further for applying a lower temperature to the sensing surface to enhance sensitivity of trace chemical detection. Above the adhesion layer, an aluminum layer **2130** with a thickness in the range of 0.5-10.0 micrometers, is deposited. Then an anneal operation is performed on the aluminum layer **145** to recrystallize the Al film.

Next, an anodization process is carried out to produce a porous structure **2140** in a form of porous aluminum oxide **2135** (FIG. **21**B). In the anodization process, the nano hole or nano rod diameter, the spacing between nano holes or nano rods, D, and the depth of nano hole array or height of nano rod array can be controlled and modified by adjusting operation voltage, current, chemical solution pH value and temperature and process time, etc. The porous structure is formed with naturally self-assembled hexagon-shaped nano pore-array that includes a plurality of pores **2140** surrounded by hexagon-shaped pore wall. Then a wet etch process is performed to widen the pores **2140** and to remove the barrier layer at the bottom of the pores.

Next, an active material such as a noble metal **2150**, such as Ag, Au, or Cu, is deposited to fill the plurality of pores by a physical, chemical, or electro-chemical method (FIG. **21**C). A chemical process is then performed to remove the top portion of the noble metal **2150** and the aluminum oxide **2135**. A plurality of noble metal columns **2155** are formed on top of the adhesion layer **2120**. The exposed portion of the adhesion layer is removed to expose the inactive SERS nano surface **2115** (FIG. **21**D). The completed device has a plurality of nano rods with the active SERS nano surfaces **2156** formed on the top and side wall surfaces of the rods. These active surfaces are surrounded by the exposed inactive SERS nano surface **2115**.

FIG. **22** shows a trace chemical detection system based on the array device in accordance with one embodiment of the present invention. The system includes surface-enhanced Raman spectroscopy (SERS), surface-enhanced Raman resonance spectroscopy (SERRS), surface-enhanced coherent-anti stokes Raman scattering (SECARS), surface-enhanced infrared absorption (SEIRA) spectroscopy, surface-enhanced fluorescence spectroscopy (SEFLS), surface-enhanced photoluminescence spectroscopy (SEPLS), time-resolved above mentioned spectroscopy, other optical spectroscopic methods, and combination of above listed methods, for example, SERS combine with SEFLS or SERS combine with SEPLS, for chemical fingerprint identification and trace chemical sensing.

As shown in FIG. **22**, a probe assembly **2200** includes an optical source **2210** such as a laser beam source and an optical assembly **2215** to focus the laser beam. The beam is then deflected by a deflector **2220** to irradiate an array device **2250**. The array device **2250** is adsorbed with a chemical substance which is going to be analyzed. Molecules **2240** of the chemical substance adsorbed on the sensing surface of the array device scatter the incoming beam **2235**. A portion of the scattered photons **2236** are collected by an optical system. A spectrum analyzer, such as a spectrometer, receives said portion of scattered photons and generates an output indicative of the composition of the chemical substance.

The system illustrated by FIG. **22** can be used in chemical fingerprint identification and trace chemical sensing in the areas of medical/health care, life science, environmental, food safety, forensic, homeland security, etc. For homeland security application at the areas including but not limited to airports, customs, cargos, harbors, trains and train stations, subways, buildings, shopping malls, theaters, resort centers, surface water and other water supply system including wells, the dangerous and harmful chemical compounds can include explosives, nerve agents, blood agents, blister agents, heavy metals and other poison chemicals, e.g., Pb, Cd, Hg, Tl, and arsenic contained compounds, volatile toxins, e.g., benzene, chloroform, pulmonary agents, e.g., phosgene, vinyl chloride, biological agents, toxins, and nuclear weapons. The explosive substances can include TNT, DNT, MNT, DNB, DMNB, EGDN, NG, RDX, PETN, TATP, TATB, HMX, ammonia nitrate, tetryl, picric acid, HNS, etc., and mixtures of two or more items mentioned above, for example, C-4, etc. The dangerous chemical substances also include nerve agents including but not limiting to tabun (GA), sarin (GB), soman (GD), Cyclosarin (GF), Lewisite and VX, etc. The blister agents can include HD (distilled sulflur mustard), etc. The tear agents, including 2-chloroacetonphenone, etc. The blood agents can include cyanides (cyanogen chloride (CK), hydrogen cyanide (AC), potassium cyanide (KCN), sodium cyanide (NaCN), etc.), arsine (SA). The blister agents can include but not limiting to lewisite, phosgene oxime (CX), mustards, etc. The biological agents can include category A agents, e.g., anthrax, *bacillus anthracis* (LD Viable), Ricin, *Yersinia pestis, Burk holderia mallei, Francisella tularensis, Brucella abortus*, smallpox, plagues, category B agents, e.g., Q fever, category C agents, e.g., yellow fever, and Severe acute respiratory syndrome (SARS) and bird flu, etc. The viruses include (but not limited to) Congo Crimea hemorrhagic fever virus, Eastern equine encephalitis virus, Japanese encephalitis virus (JEV), yellow fever virus (YFV), Ebora virus, Equine morbillivirus, Lassa fever virus, Marburg virus, Rift Valley fever virus, South American hemorrhagic fever virus (Junin, Machupo, Sabia, Flexal, Guanarito, etc.), Tick borne encephalitis virus, smallpox virus, virus which can cause Hantavirus pulmonary syndrome; bacteria include (but not limited to) Anthrax bacillus, Cattle, sheep, swine brucellosis, Burke Holder of glanders bacteria (*Pseudomonas mallei*, etc.), *Clostridium botulinum*, Turafrancisrand, the plague *bacillus*, etc.; *Rickettsia* include (but not limited to) *Q Rickettsia, Rickettsia prowazekii* (Cause typhus), *Rickettsia rickettsii*, etc.; Fungus include (but not limited to) *Coccidioides immitis*, etc.; toxins include (but not limited to) Abrin, Aflatoxin, Botulinum toxin, *Clostridium perfringens* toxin, Conch toxins, Two acetyl grass sickle enol toxin, Ricin, Shellfish toxins, Shiga toxin, *Staphylococcal enterotoxin Staphylococcal enterotoxin*, Tetrodotoxin, T-2 toin, etc.

The system based on the array device in accordance of the present invention can also be used in chemical fingerprint identification and trace chemical sensing in environmental application, for example, toxic materials monitoring and screening, including but not limited to inorganic, organic, nitrites and chlorine contained chemicals, such as $NO_2^-$ and $ClO_4^-$ groups and dioxins, benzene, aromatic group and its derivatives, cyanides, heavy metals including but not limited to Pb, Cd, Hg, $Cr^{6+}$ and arsenic contained compounds, and residue pesticides, insecticides, herbicides, and other toxic chemicals in ocean, lake, rivers, reservoir, and wells, and other surface and underground water, as well as in soul and in air.

For environmental protection, the disclosed chemical sensing system can be used for outdoor and indoor pollution monitoring and screening emission sources. Outdoor pollution includes auto vehicle exhaust gas, factory exhaust gas and liquid, etc. Indoor pollution monitoring and screening in both family houses and workplaces, including but not limited to building, airplane, space shuttle, boat and ship, submarine, and all other areas under the ceiling. Application includes but not limits to monitoring and screening air quality and other health problems associated with plastic floor, wall painting and decoration, painted furniture, plastic household, tools, toys and all other plastic materials indoor which may contain toxic materials, for example, benzene, its derivatives and other volatile organic compounds (VOC), polyvinyl chloride (PVC) and its plasticizer additives including phthalate, DEHA family, and heavy metals, etc.

For medical applications, non-invasive or minimal-invasive early disease screening test and diagnosis can be accomplished using the disclosed array device in accordance of the present invention. For example, test through human skin test, eye test, or body fluid test, including saliva, sweat, blood, and urine test, and human breath test to early detect diseases, including but not limited to lung cancer, breast cancer, oral and head cancers, ulcer, bronchial, oesophageal and stomach cancer, colon cancer, skin cancer, diseases of liver, kidney, pancreas, bladder, prostate, uterine, esophageal disease, oxidant stress, eye disease, diabetes, schizophrenia, lipid peroxidation, asthma, tuberculosis, helicobacter pylori, etc. Noninvasive or minimal-invasive test can be also applied to screening test and diagnose Alzheimer's disease.

The disclosed systems and methods are applicable to urine test by "Smart Toilet" equipped with SERS sensor to early detect diseases, including but not limited to prostate cancer, diseases of bladder, uterine, etc., and to monitoring and screening illicit drugs.

The disclosed systems and methods are applicable to human and animal body fluid test. For example, saliva test for oral cancer, blood test for early disease screening test or diagnosis, including but not limit to Alzheimer's disease, Parkinson disease, HIV, mad cow disease, cardiovascular disease, cancers, and rapid pathogen, virus or bacteria, identification and screening, including but not limited to SARS, bird flu, smallpox, HIV, anthrax, ricin, etc.

Raman screening test and diagnosis method can be applied to real time doctor visiting procedure, such as disease screening or special disease diagnosis. In this way, doctor is able to make judgment based on real time Raman test during patient visit, and make on timely decision for necessary medical treatment.

The disclosed systems and methods can be used during surgery, real-time in-line identify cancer tumor portion, rather than usually applied biopsy method which requires time, distinguish the boundary between cancer tumor portion and health portion to real-time support doctor to make decision on cutting location.

The disclosed systems and methods can be used in pharmaceutical applications in medicine R & D, manufacturing and quality monitoring. Raman method can be also applied to medical treatment, for example, medicine taking feedback process, surgery, Chemotherapy, Radiotherapy, etc. For example, before a medical treatment, like patient taking medicine and after patient taking medicine at different period of time, Raman test can be carried out to investigation effectiveness from medicine, then the result can be fed back to a doctor to modify prescription type and dose for the best medical treatment to different patients, respectively, with different level of medical treatment metabolism efficiency level.

The disclosed systems and methods are compatible with a miniaturized Raman sensor with wireless technology used inside human body. For example, a system-on-chip Raman system can be made in a tablet size which includes on-chip mini-laser source, MEMS based mini-spectrometer, wireless module, mini-probe, etc. Initial application will be disease screening test and diagnosis of digest system. For example, patient or a person being screened swallows a tablet sized Raman system after his/her digest system got cleaned (similar procedure to that of preparation for colon endoscopy test). Raman scans will be taken timely, for example, from every one minute to every hour a time. Then data will be transferred by wireless module, and a computer outside human body will receive Raman data and analyze, search, match, and decision making. The next stage of application is minimal invasive with a needle shaped probe head to bring mini-Raman sensor into diagnosis area inside human body. Raman data can be transferred through optic fiber, or wireless module. Applications include but not limit screening test and diagnosis of breast cancer, Alzheimer's disease, etc.

The disclosed systems and methods can be used in biotechnology and biomedical applications, such as fingerprint identification of DNA, RNA and protein, DNA sequencing, DNA sorting, etc.

The disclosed systems and methods can be used in forensic applications such as drug test and screening through saliva test, urine test, or powder test; false signature recognition; human identification and screening by DNA profiling; identify microscopic paint fragments, fiber identification, etc. The disclosed systems and methods can be used in drug screening through human body fluid test, or/and breath test by Raman method based on the array device in accordance of the present invention is developed.

The disclosed systems and methods are applicable to food, fruit and beverage monitoring and screening application, monitoring of chemicals in gas, liquid, power, gel, aerosol, or solid phases, including but not limited to ethylene, for stored fruits and vegetables with longer shelf time application; food safety, monitoring and screening harmful chemicals including but not limited residue pesticides (e.g., methamidophos, cypermethrin, deltamethrin, malachite green, etc.), dioxins, illegal artificial additives (e.g., Sudan I, Sudan II, Sudan III, Sudan IV, etc.), food processing by-products (e.g., acrylamide formed from potato chips from processing temperature over 120° C.) by Raman method based on the array device in accordance of the present invention is developed. Those chemicals include but not limit to acrylamide, malachite green, etc. Foods under investigation include but not limit to potato chips, French fries, fried potato, potato crisps, cookies, crackers, cereal products, crisp bread, bread, coffee, prepared toast, roasted nuts, biscuits, chocolates, popcorn, and aquatic products including fish, etc.

The disclosed systems and methods are applicable to identifying and monitoring food packaging processing and preparation materials, including but not limited to identify and screen polyvinyl chloride (PVC) and phthalate materials used as the microwave food wrap, kitchen film, food packaging, processing and preparation materials.

The disclosed systems and methods are applicable to screening counterfeit merchandizes and materials, including but not limited to medicines, drugs, milk-based powders, edible oil, wines, gemstones, currency bills, false signature through inks, art pieces, gasoline, etc.

The disclosed systems and methods are applicable to industrial process quality and production safety monitoring. Application areas include but not limited to process control for product quality, process and production safety at gas and wet chemical process lines, for example, petroleum refinery plant, chemical engineering manufacturing plant, semiconductor wet chemical process line in clean room, airline and space shuttle, boat, ship and submarine, etc.

The disclosed systems and methods are applied to determine the locations of chemicals. For example, a sensor or sensor network can be placed at different locations including but not limiting to medical doctor clinic office, surgery operation room, shopping center, public resort area, building, custom, road check station, harbor, airport, vehicle, boat and ship, airplane, space shuttle, industrial process site, R&D research lab, quality control office, college lab and office, surface water, well, ground water, hand carried by operation people, and so on.

Chemical sensing application engineering, not only single chemical sensor is placed on site, but chemical sensor network is designed and arranged to cover application area which all sensors are controlled by sub-central controllers and main-central controller connected with fiber optic or/and wireless system. When abnormal result is found, an alarming signal is automatically triggered in the forms including but not limiting to red color blinking on screen of a computer or PDA, alarming sound in key area, sending alarming E-mail to key people, triggering a phone call to key people cell phone, etc. The abnormal result can be classified into different risk level, for example, green (safe), blue, yellow, orange, red (the most risk).

## EXAMPLES

The disclosed system and methods are further described in the following examples, which do not limit the scope of the invention described in the claims.

### Example 1

### Fabrication of Nano-Surface Arrays by Anodization Method

A thin film of Ti (about 100 nm) was deposited by e-beam evaporation of Si (100) wafer, followed by the deposition of Ag (about 100 nm). Then a 500 nm Al layer was deposited over the Ag film using physical vapor deposition method.

Then the coated Si wafer was placed into an anodizing bath with 0.3 M oxalic acid solution as the electrolytic solution. The bath was maintained at 10° C., and the anodizing voltage was set at 35 V. After anodization, nano-size narrow pores were formed in the $Al_2O_3$ layer. The diameter of the pores (or holes) can be widened by placing the wafer into a 10 wt. % phosphoric acid solution. The nano pore structure in the $Al_2O_3$ layer acted as a mask for etching active metal layer or depositing active metal layer. Thus a nano surface array was formed after removing oxidized Al layer.

Example 2

Nanoimprint Lithography for Fabrication of Nano-Surface Arrays

The first step in nanoimprint is to press a mold into a thin resist cast on a substrate. The step is to duplicate the nanostructure on the mold in the resist film. The second step is to etch the resist film to form the nanostructure on the substrate.

The mold was patterned with an array of nano dots of 30 nm in feature size using electron beam lithography and reactive ion etching (RIE) on a Si wafer. PMMA was used as the resist on Au coated Si (100) wafer. A thin Ti layer was inserted between Au and Si to improve adhesive. The imprint process was carried out in vacuum at a temperate around 160° C., above the glass temperate of PMMA, at a pressure about 1000 psi. After the pattern from the mole was transferred to the Au coated Si (100), oxygen RIE was used to remove residue resist in the compressed areas in PMMA. Then, the pattern was etched into the Au film. After removing the PMMA, a nano-hole array was formed in Au.

Example 3

1) Demonstration of Nano Array

FIG. **24** is an example of scanning electron microscopy imaging of such nano surface arrays. The left image shows an array of nano-holes with 17 nm diameter and about 30 nm spacing. The image on the right shows an array of nano-holes with 38 nm diameter and about 10 nm spacing.

2) Demonstration of Surface-Enhanced Raman Using the Nano-Surface Arrays

A Raman scattering system, as shown in FIG. **23**B, includes a Raman nano-surface array on silicon, a semiconductor laser, which can collect the reflected lights on the surface. The sampling methods include: the array is placed in a solution container or a gas probe cell; or is just lie down horizontally, then to inject liquid chemical onto the surface; or the array is covered by a layer of glass or polymer without physical contact, liquid or gas sample is injected through a microfluidic channel.

FIG. **23**C shows Raman spectra of xylenes. In this example, Raman spectrum of m-xylene, o-xylene, p-Xylene, and mixed xylene are demonstrated separately. As shown in FIG. **23**C, each chemical has its own chemical spectral fingerprint, even though the mass of those different xylenes are exact the same. On the other hand, Raman spectrum of mixed xylene shows little interference among those 3 different xylenes. Then, each chemical can be distinctively identified, therefore, Raman methods is one of the best chemical identification ways with spectral fingerprint capability.

Another experiment was carried out using methamidophos (MAP) which is a key pesticide; nerve agent stimulant. A trace amount of the chemical is introduced in liquid phase and vapor phase, respectively. The SERS spectra of these samples are compared against normal Raman spectrum of a pure MAP solid sample. As shown in FIG. **25**, both liquid sample and vapor sample show MAP spectrum signature. It demonstrates that MAP vapor detection sensitivity is better than 40 parts per billion (ppb).

Monitoring Network System

In some embodiments, a monitoring network system **2600** includes a central office **2610**, a mobile detector **2620**, and an analysis lab **2630**. The central office **2610** can be operated by a government responsible for food safety, environment monitoring and protection, public health, public security, and crisis preparation and warning agencies, etc. The central office **2610** can be run an independent institution that manages quality control for industrial production of food, drinks, medical drugs, petroleum products, and other industrial products, distribution center for commercial products, etc. The mobile detector **2620** can include a portable detector carried by inspection personnel, or a detector system on a vehicle, which are suitable for collecting and detecting harmful substances in the field. The mobile detector can be positioned at distribution centers for food and other commodities, grocery stores, shopping malls, cinemas or sport facilities, or inspection stations on highways, or at border control, airports, bus stations, subways, and train stations, etc. The mobile detector **2620** includes a probe **2621** and an ID reader **2625**.

The mobile detector **2620**, as shown in FIG. **27**, can include a probe head **2720** and a sensor **2730** positioned adjacent to the probe head **2720**. The sensor **2730**A includes nano-structured surfaces that can adsorb molecules of the substance in the sample or in the ambient environment. The nano-structured surfaces in the sensor **2730** can include an array of active SERS nano surfaces and inactive SERS nano surfaces on a substrate or nano particles on a substrate surface, or the nano particles in a test reagent, as disclosed above in relation to FIGS. **1-25**, and FIGS. **30-33** below. The sensor **2730** can also include nano particles in a solution, wherein the sample is introduced in the solution to allow sample molecules to be adsorbed onto the nano particles. The probe head **2720** includes a compact laser **2721** (e.g. a semiconductor laser) configured to illuminate a laser beam on the sample molecules adsorbed on the sensor **2730**. The probe head **2720** further includes collection optics **2722** that can collect light scattered from the sample molecules adsorbed on the nano-structured surfaces. The scattered light comprises information about the sample molecules. The probe head **2720** can also include a compact spectrometer **2740** configured to produce a spectrum of the scattered light collected by the probe head **2720**. The spectral data is output from the spectrometer **2740** to a wireless communication circuit **2745**. The wireless communication circuit **2745** can include an RF transceiver, one or more amplifiers, and impedance matching circuit. The wireless communication circuit **2745** is coupled to an antenna **2711** configured to transmit the spectral data to the central office **2610** via a wireless network **2628** (FIG. **26**). The communication can be encrypted in secure protocols.

The ID reader **2625** can be in different formats such as includes non-contact reader such as RFID reading device, a mobile phone, a camera phone, a barcode scanner, an image object recognition system, and a computing device dedicated for inspection and monitoring purposes, etc. The ID reader **2625** can be integrated with the spectrometer **2740** and the probe head **2720**, or standalone and in wired or wireless communication with the wireless communication circuit **2745**. In some embodiments, the wireless communication circuit **2745** is integrated with the ID reader **2625** (and the display **2750**). The spectrometer is connected or in wireless communication with the ID reader **2625**.

The ID reader **2625** can receive identification information about the sample such as product model number, batch number, the location of the sampling and substance detection, information about the source of the sample such as the original farm or ranch where the food come from or the manufacturer of a food product, carrier information (e.g. vehicles, trains, ship, airplanes) and the destination of the sample material. The identification can be received in the forms of 1D barcodes, 2D barcodes (i.e. matrix code), alphanumeric numbers, text, etc. The sample ID information is transmitted to the central office **2610** in conjunction with the spectral data of the respective samples. The ID reader **2625** can also receive from the carrier, distributor, or manufacturer of the sample information about pesticide and insecticides applied on the foods being detected, information about animal feeds and antibiotics used on inspected animals and poultries (meat and eggs) and water products.

The mobile detector **2620** can include a display **2750** for displaying instructions for conducting the spectral measurements and messages from the central office **2610**. The mobile detector **2620** can include a digital or video camera **2760** which can be combined with the ID reader **2625** or as a separate device. The camera **2760** can take a picture of the commodity that contains the sample material, the vehicle's license number that carries the sample material, the sample or product ID, the driver's license etc. The camera **2760** can also continuously take video images of a site to detect suspicious personnel in correlation with the detection of the harmful materials.

The mobile detectors **2620** can be located within a short range (e.g. within hundreds of yards or a couple of miles) from the central office **2610** to allow wireless signals comprising the spectral data to be communicated in a wireless protocol such as WiMax, WiBro, WiFi, WLAN, 802.11, 802.16, and others. The mobile detectors **2620** can also be located at a long distance from the central office **2610**, wherein the wireless signals comprising the spectral data can be communicated using wireless communications standards and protocols such as 3G, 4G, Global System for Mobile communications (GSM), Universal Mobile Telecommunications Service (UMTS), and Code Division Multiple Access (CDMA). GSM can include GPRS, EDGE and CSD. UMTS can include Wideband Code Division Multiple Access (WCDMA), High-Speed Packet Access (HSPA), High-Speed Downlink Packet Access (HSDPA), UMTS-TDD, and Long Term Evolution (LTE). CDMA can include CDMA2000, and Ultra Mobile Broadband (UMB).

Referring to FIG. **26**, the analysis lab **2630** can be used for detailed analysis or harmful substances collected from the field or at a large industrial manufacturing sites or distribution center where a high volume of samples need to be analyzed. The analysis lab **2630** can include one or more probes **2631** and one or more ID readers **2635**. The probe **2631** and the ID reader **2635** can have structures similar to those illustrated in FIG. **27**. The probe **2631** and the ID reader **2635** can communicate with and send spectral data and sample ID information of the samples to the central office **2610**.

In some embodiments, referring to FIG. **28**, a network of probes can be positioned at grocery stores, shopping malls, transportation stations, border control, a check station on a road, a harbor, an industrial site, a school, or a water source, etc., as described above. Each probe includes a sensor and a probe head. The sensor includes nano structured surfaces to which the molecules can be adsorbed. The probe head is configured to emit a laser beam and collect scattered light from the molecules collected by the sensor. The probe can include a spectrometer for producing spectral data such as Raman spectrum from the scattered light. An ID reader can receive identification information about the sample, the manufacturer, the distributor and carrier of the sample, and/or the destination of the sample.

The sensors in the network capture substances from samples or their perspective environment (step **2810**). The samples can include food, drinks, medicine, materials used or produced in manufacturing, water, air, and soil samples from the environment, and samples for forensic and security examinations. The harmful or hazardous substance can include unauthorized additives, residues of pesticides, insecticides and antibiotics in food products, illicit drugs, explosives and flammable materials, a poisonous gas and other harmful chemicals, and contagious virus and bacteria.

Specifically, the sample material can be extracted from a food product such as dairy products, candies, cookies, drinks, alcohol, meat, seafood, tea, fresh or canned vegetables, fruits, grain products, cereals, corn chips, potato chips, or protein containing food. The dairy products can include milk, milk powders, cheese, cheese-containing cakes, yogurts, ice creams, milk containing candies, or cookies, wherein the harmful substance includes melamine, melamine cyanurate, sodium cyclamate, sodium cyclohexylsulfamate, cane sugar, starch, nitrite, nitrate, sulfide, Sudan I, II, III and IV, malachite green, methomidophos, acephate, DDT, DDV, malathion, fenitrothion, malathion, malathion, carbofuran, brodifacoum, tetramethylenedisulfotetramine, sodium fluoroacetate, fluoroacetamide, chlorphacinone, pindone, diphacinone, amitraz, monocrotophos, phorate, disulfoton, phosmet, parathion, fenthion, phosphamidon, diazinon, aldicarb, trichlorfon, aldrin, bentazone, deltamethrin, cypermethrin, methyl parathion, phosmet, dimethoate, nitrofuran, furanzolidole, chloramphenicol, chlortetracycline, ciprofloxacin, clenbuterol, ractopamine, enorfloxacin, rhodanmine B, benzoic acid (sometimes found in milk products), hyposulfurous acid, sodium formaldehyde, formaldehyde, phthalates, dioxins, Pd, Cd, Hg, As, and Cr in water, cyanides, chlorates, sulfates, crysoidine G, boric acid and borax, sodium sulfocyanate, lead chrome green, Basic Flavine O, industrial used formaldehyde and NaOH, carbon monoxide, sodium sulfate, industrial surfer, industrial dyes, fructus papaveris, over dosed level of food colorants (e.g. carmine, lemon yellow, allura red AC, sunset yellow, etc.), food preservants, sweeteners (e.g., saccharin sodium salt, Sodium cyclamate), emulsifier (sucrose easter of fatty acid, etc.), swelling agents overdose ($KAlSO_4$, $NH_4AlSO_4$, etc.), bleach, sulfer suffumigation, color protectants (nitrate, nitrite, etc.), $TiO_2$, benzoyl peroxide, olaquindox, chloromycetin, and $KAlSO_4$.

Molecules of the captured substance are adsorbed on the nano structured surfaces of the sensors. The sample identification is next obtained (step **2820**). The sample identification can include information that identifies the sample, and the source, distribution channel and method, and the destination of the sample.

Spectral data are next obtained from the molecules adsorbed to the nano structured surfaces of the sensors (step **2830**). As described above, a laser beam is emitted by a laser in the probe assembly (such as the one shown in FIG. **22**) to illuminate the molecules adsorbed on the nano structured surfaces on a sensor or in a sample solution. Light scattered by the molecules is collected by the probe assembly. The spectral data is obtained from the scattered light by a spectrometer in the probe assembly. An example for the spectral data is Raman spectrum. The nano structured surfaces on the sensor provide surface enhancement to the signal intensity in the Raman spectrum. The substance capture and associated spectral data can be conducted per sample, or periodically (e.g. at 1 min, 10 min, 15 min, or 1 hour intervals).

The spectral data and the sample identification are next transmitted from the sensors to a central office (step **2840**) in wired, wireless or other medium. Referring to FIGS. **26** and **28**, the central office **2610** can include a communication device such as a server **2640** configured to communicate with the mobile detector **2620** and the analysis lab **2630**. A controller **2650** can handle the data to and from the mobile detectors **2620** and the analysis lab **2630**, and can control various tasks for a spectral analyzer **2660**, a database **2670**, the alert and response system **2680**, and a qualification system **2690** under predetermined guidelines or policies stored in the database **2670**.

The database **2670** stores spectral signatures in association with harmful substances. The spectral analyzer can identify the spectral signatures of known harmful substances in the spectral data, which determines the existence or non-existences of the harmful substances in the samples (step **2850**). The results of the spectral analyses are stored in the database **2670** in association with their respective sample IDs under the control of the controller **2650**. The database **2670** can store records for different manufacturers, producers, distribution channels, retailers, grocery stores, etc. Problematic entities or locations can be checked more frequently.

If one or more spectral signatures associated with a harmful substance are found in spectral data, the harmful substance is identified in the sample of a product (step **2850**). The result is stored in the database **2670**. The controller **2650** can ask the analysis lab **2630** to confirm the finding. The controller **2650** can direct the alert and response system **2680** to send out alerts to operators, the mobile detectors **2620** and other mobile devices in the field, to the check points of the distribution channels for the sample products, to the destination of the sample product, or the manufacturing location of the sample product (step **2860**). The alert messages can be displayed on the display **2750** in the mobile detector **2620** so that the in-field operator can take appropriate actions such as stopping the shipment of the lot of material containing the detected harmful material. The warning signal can be in the form of emails, text messages, and voice phone call, etc.

The alert and response system **2680** can generate a "high-risk target list" for the detected harmful substance and base materials, and transportation vehicles, distribution channel and production source associated with the detected harmful substance. The "high-risk target list" is stored in the database **2670** to allow the monitoring network system **2600** to more frequently monitor samples on the "high-risk target list" afterwards.

The level of urgency can be categorized by different risk levels such as green (safe), blue, yellow, orange, red (the most risky). The warning signal can include the current and/or anticipated position of the hazardous substance as well as the suspected exterior appearance for the carrier or the package for the hazardous substance. Appropriate personnel can be alerted. Security personnel can be dispatched to the location of the hazardous substance. An evacuation can be initiated.

If a harmful substance is not found in the samples of a product, the qualification system **2690** can qualify the sample as clear of harmful substances; the results can also be stored in the database **2670** for the record (step **2870**).

In some embodiments, the location and time of the hazardous/harmful substance can be correlated by the positions of the sensors and the capture times for the detections of harmful substance. The location for a stationary hazardous material can be determined by interpolating the positions of the sensors. The locations and capture times of a moving sample containing the hazardous substance can be generate a moving path to predict the destination of the sample to allow it to be intercepted.

In some embodiments, the spectral data collected by the sensors can be used in conjunction with image data captured from the scene near the spectral sensors. For example, a digital or video camera **2760** positioned near the probe can take a picture of a suspected person or a package. The image of the suspected person or package can be stored and reported in association of the location of the hazardous substance to prepare for an appropriate response.

The above disclosed systems and methods have wide applications. In one example, a distribution center for meat, vegetables, fruits, and other food products can include a central office (as shown in FIG. **26**) and multiple inspection personnel each carrying (or wearing) a mobile detector. The distribution center can include an analysis lab or can use the services of an analysis lab off site. The food products such as vegetables, dairy products, meat and vegetables can be shipped into the distribution center by big trucks (e.g. 20 ton trucks) from food manufacturing sites, vegetable, orchards, farms, dairy farms, ranches, etc. The inspection personnel can retrieve the identification of each food product, driver and vehicle information, and the source and destinations of the product. The inspection personnel can visually inspect the food product, and take samples of the incoming food products for spectral detection as the products are offloaded from the big trucks. The identification information and the spectral data are wirelessly transmitted instantaneously to the central office for spectral analysis. The data is stored in the database. The food products that pass the inspection will be qualified. The food products are then separated into small batches and loaded onto smaller trucks (e.g. 2 ton trucks) to be shipped to retail sites such as grocery stores, supermarkets, restaurants, and large retail stores such as Costco, Wal-Mart, or Target. The problematic products can be held for further analysis in the analysis in the lab. If harmful substance is confirmed, the food products can be stopped or destroyed. Since the identification information is stored, the source of the food is immediately known. Inspection personnel can be sent to the site that produced the food product, and alert messages can be sent to other distribution centers that may have received food products from the same source.

In another example, the disclosed monitoring system can be used to monitor and to prevent the spread of infectious diseases such as SARS in wide area. The disclosed monitoring system can be used to monitor pollutants in the environment, and to monitor chemical and biological agents for preventing and defending against terrorist attacks. For example, the disclosed monitoring system can be disposed in a water distribution system including reservoirs, canals, water treatment plants, and rivers. The disclosed monitoring system can be used to sense chemical changes in the environment for forecasting earthquakes or monitoring chemical changes for action taken after earthquakes.

In some embodiments, the probe **2621** in the mobile detector **2620** and the probe **2631** in the analytical lab **2630** can include other types of sensors. For example, the probe **2621**, **2631** can include a chemical or biological immunoassay for detecting harmful biological and chemical substances. The biological immunoassay is configured to hold a plurality of antibodies which each is specifically configured to bind with a target antigen which may be part of or associated harmful biological and chemical substance. Likewise, the biological immunoassay can hold a plurality of antigens which each is specifically configured to bind with a target antibody which may be part of or associated harmful biological and chemical substance. The binding of a specific pair of antigen-antibody in the biological immunoassay can be detected by spectral analysis such as Raman spectroscopy as a positive identification of the harmful antigen or antibody substance. A spectral signature can indicate the binding of one of plurality of antibodies with the specific antigen.

In another example, the probe **2621** in the mobile detector **2620** and the probe **2631** in the analytical lab **2630** can use enzyme inhibition method. Vegetables often include residuals of pesticides which may include organic phosphorus Inhibition of enzymes by the organic phosphorus can be detected by spectral analysis such as Raman spectroscopy. A spectral signature can indicate the inhibition of the enzyme by a harmful substance in the sample material, which is used as an indication to detect the residual pesticides in vegetables and fruits. In some embodiments, referring to FIG. **29**, a monitoring network system **2900** can include a network of central offices **2600**, **2600**A, **2600**B . . . , each in communication with mobile detectors **2620** or stationary detectors. The monitoring network system **2900** can include one or more analysis lab **2930** in wired or wireless communication with the central offices **2600**, **2600**A, **2600**B . . . . The monitoring network system **2900** can include a central database to track inspection data from all central offices **2600**, **2600**A, **2600**B . . . so that the data can be cross shared between the central offices which can cover a large region such as a a state, a province, a country, a district, a city, an inspection station or a mobile vehicle. The controllers and processors in the central offices **2600**, **2600**A, **2600**B . . . can process data in a cloud computing model. The qualification and warning can be implemented in region wide. A region-wide alert and response system is in communication with the plurality of central offices. The alert and response system is configured to send out an alert signal about the sample material when the harmful substance is identified in the sample material in one or more of the central offices.

The monitoring network system **2900** can include different stages of inspections: the first stage inspection of harmful substances: using on-site and high throughput detection methods, such as Raman and surface-enhanced Raman methods, enzyme inhibition method, and chemical or biological immunoassay method, to screen high volume high distribution-rate goods (for example: food, drinks, water, drug raw materials, body fluid samples of human being or animals, etc.) in distribution channels, storage areas and logistics distribution centers. Small quantity of the samples (e.g. 0.1%-1% of the samples) can be sent to the analytical lab **2630**. The analytical lab **2630** can have other lab equipment such as HPLC, GC-MS, IC, IMS, AAS, ICP-MS, etc., for additional analyses for confirming the existence of the harmful substance.

The monitoring network system **2900** can include different authorized levels: a first level at inspection point (test station or inspection mobile vehicle), a second level that connect inspection points at the first level by a network, a 3$^{rd}$ level of city monitoring and control center, a 4$^{th}$ level of county monitoring and control center, a 5$^{th}$ level of the province/state monitoring and control center, and a 6$^{th}$ level of central government monitoring and control center. The monitoring network system **2900** can track the detected harmful substance back to its distribution channels and production sources, so that event monitoring and control center is able to find impact channels and areas as function of time, in order to take immediate action to minimize impact from the event.

Detecting Crude Oil or Gas Content in Drilling Samples Using Nano Surface-Enhanced Raman Spectroscopic Analysis Method

The increased energy consumption requires low cost, effective and efficient ways to explore crude oil and gas under the ground. The current conventional analysis methods based on X-Ray and gas chromatography are usually conducted in the labs and have long turn-around times. The present application discloses Raman spectral analyses methods for detecting crude oil and gas in drilling samples extracted from wells. The disclosed methods are at least as accurate as conventional methods, and can be conveniently implemented in the field with significantly reduced measurement cycle times. The disclosed systems also have lower cost than conventional measurement systems.

To detect potential crude oil or gas underground involves drilling a deep hole (e.g. in about 10 cm diameter) into the ground with a drill bit, and extracting a drilling sample (i.e. drilling record) that is typically in the form of a fluid or a piece of rock. For example, a drilling sample can contain a mixture of brine (e.g. about 50%, or 80%), clay and polymers (e.g. about 5%), mineral particles (e.g. about 10% or 20%), and other substances (e.g. about 5%). Once a sample out above ground, the drilling sample fluid is poured into a container, e.g., a bottle, which is subsequently sealed and shipped to a lab for testing. The drilling and pressure in the drilling process deep underground create a lot of heat, which can raise the drilling fluid to 50° C.-80° C., vaporizing much of the low molecular weight substances in the drilling fluid before they arrive at ground surface for testing. Since many low-molecular weight substances in gas and crude oil have vaporization temperatures below 100° C. or even below 20° C., the conventional crude oil/gas detection methods often do not have sufficient signal strengths for low-molecular weight crude oil/gas substances which is consistent with a sample underground (e.g., 3000 m deep underground).

In some embodiments, referring to FIGS. **30** and **31**, a drilling sample **3110** is extracted from a drilling hole (or well) in the field (step **3010**). An example of an important signature chemical substance for crude oil in a drilling sample is an aromatic compound, e.g., thiophene group including thiophene, dibenzothiophene (DBT) and its homologue molecules.

In some embodiments, referring to FIGS. **30** and **31**, a drilling sample **3110** is extracted from a drilling hole (or well) in the field (step **3010**). An example of an important signature chemical substance for crude oil in a drilling sample is an aromatic compound, e.g., phenanthrene group including phenanthrene, methylphenanthrene and its homologue molecules.

In some embodiments, a drilling sample **3110** is extracted from a drilling hole (or well) in the field (step **3010**). An example of an important signature chemical substance for crude oil in a drilling sample is an aromatic compound, e.g., carbazole group including carbazole and its homologue molecules.

The vapor pressure of thiophene, dibenzothiophene, phenanthrene, methyl phenanthrene, carbazole, and their respective homologue compound molecules is above 200° C., or 300° C.

The drilling sample **3110** is introduced into a sample solution test reagent **3120** comprising nano particles **3140** in a container **3130** (step **3020**). The container **3130** can be an optical vial, a beaker, or a transparent test tube, etc. The nano particles **3140** can exist in the form of a colloidal suspension in the sample solution **3120**. The nano particles **3140** can be in different shapes and can include carbon nano tubes. A drilling sample **3110** is prepared in chemical and physical ways including but not limited to sample purification, extraction, separation, then is mixed and/or dissolved in the sample solution **3120** to allow molecules in the drilling sample **3110** to adsorb on surfaces of the nano particles **3140** (step **3030**).

The nano particles **3140** can exist in round or irregular shapes. The nano particles **3140**, as shown in FIG. **32**, can be individually separated, or aggregated in clusters, in the sample solution **3120**. The nano particles **3140** can have a size distribution, as shown in FIG. **33**, which is characterized by an average particle dimension $d_a$ and a particle-dimension distribution width $d_w$. The ratio $d_w/d_a$ can range from about

0.01 to about 3, which defines a quite monodispersed distribution to a polydispersed particle distribution. The ratio $d_w/d_a$ can often range from about 0.03 to about 1. The average particle dimension $d_a$ can range from about 1 nm to about 10,000 nm, or from 2 nm to 500 nm.

The nano particles **3140** can be formed by materials that can be select to enhance Raman spectral signals from the molecules adsorbed on the nano particles **3140**. For example, suitable materials for the nano particles **3140** include metallic materials such as Al, Ag, Au, Cu, Fe, Co, Ni, Cr, Zn, Sn, Pd, Pt, and their alloys, oxide materials such as titanium oxide, silicon oxide, and zinc oxide, tin oxide, silicon, silicon oxide, and polymeric materials. The nano particles **3140** can also include polymers tethered to the particle surfaces to help repel each other in the sample solution **3120**. The magnetic or ferromagnetic materials (e.g. Fe, Co, Ni, or Fe, Co, Ni containing compounds, or their alloys) can enhance the Raman spectral signal when the sample solution **3120** is applied with a static or alternating electrical, magnetic, or electro-magnetic field.

In some embodiments, the sample solution **3120** can include a mixture of nano particles of different material compositions. For example, the nano particles can include a mixture of silicon and metallic nano particles, or a mixture of silicon and polymeric nano particles, or a mixture of silicon, metallic, metallic oxide, and polymeric nano particles. Raman signal intensity can be enhanced by optimizing mixture compositions.

In some embodiments, the nano particles **3140** are charged and repel each other in the sample solution **3120**, which helps to separate the nano particles **3140** and the formation of a colloidal suspension. The solvent in the sample solution **3120** can be arranged to enhance Raman spectral signal intensity from molecules adsorbed on the nano particles **3140**. It was found that ions and especially multi-valence ions can significantly enhance the signal intensity of the Raman signal. An ionic material can thus be added to the sample solution **3120**. Examples of ions that the ionic material carries to the sample solution **3120** can include $Na^+$, $K^+$, $Li^+$, $Ca^{++}$, $Ba^{++}$, $Sr^{++}$, $Mg^{++}$, $Mn^{++}$, $Al^{+++}$, $Zn^{++}$, $Sn^{++}$, $Sn^{++++}$, $F^-$, $Cl^-$, $Br^-$, and $I^-$, and so on. The ions can have mono charge, or preferably have double or high charges in the sample solution **3120**. The ions can have positive or negative charges. The sample solution **3120** can have an ionic compound, including but not limited to LiF, NaF, NaCl, KCl, KI, etc. Suitable ionic concentration can range from 10 μM to saturated level.

In some embodiments, the nano particles **3140** can include carbon nano tubes with diameters ranging from 0.3 nm to 100 nm. The lengths of the carbon nano tubes can be from 5 nm to multiple millimeters. The length-to-diameter ratio of the carbon nano tubes can be as high as 50 million. The carbon nano tubes can have single-walls, or multiple walls. The carbon nano tubes can be in the form of Fullerite, a torus, nanobuds, and nanoflowers.

A probe **3150** includes an optical transmitter (e.g. a laser device, not shown) and an optical detector (not shown). The optical transmitter emits an incident light **3151** (e. g. a laser beam) to illuminate the nano particles **3140** and the molecules adsorbed on the nano particles **3140** in the sample solution **3120** (step **3040**). Scattered lights **3152** from the nano particles **3140** and the adsorbed molecules are collected by the optical detector in the probe **3150** (step **3050**). The output signal from the probe **3150** is analyzed by a spectral analyzer **3160**.

Optionally, when the nano particles **3140** are made of magnetic materials, an electrical field, a magnetic field, or an electro-magnetic field is applied to the sample solution **3120** when the scattered light collected.

An important aspect of the presently disclosed method is that the steps of illuminating the sample solution and collecting light scattered by the drilling sample can be conducted in the field, that is, in the vicinity of the drilling hole to carry out on-site test. There is no need to ship the drilling sample to a central lab location. Thus testing cycle time is saved in the presently disclosed method not only in the measurements themselves but also in the eliminating the time spent on shipping the drilling samples.

A Raman spectrum of the molecules adsorbed on the nano particles **3140** is obtained from the scattered light (step **3060**). For example, as shown in FIG. **34**, nano-surface-enhanced Raman spectra (or nano-enhanced Raman spectra) are obtained from drilling samples extracted at different depths (2100 meters to 2458 meters) of a drilling hole. The spectra corresponding to different drilling-hole depths show several Raman spectral peaks about 540 $cm^{-1}$, 586 $cm^{-1}$, and 1350 $cm^{-1}$.

Spectral signature(s) in the Raman spectrum can be used to identify the molecules adsorbed on the nano particles (step **3070**). The concentration of the substance associated with the spectral signature in the drilling sample can be calculated using the spectral signature. For example, the height of a spectral peak, or the area under a spectral peak, or a signal-to-noise (i.e. peak to background noise) ratio can be calculated to calculate the concentration of the substance in the drilling sample. Since crude oil or gas is known to contain the substance, crude oil or gas content in the drilling sample can be qualitatively and quantitatively determined (step **3080**). Steps **3070-3080** can be conducted by a local spectral analyzer **3160**, or remotely in a central office that in communications with the probe **3150** as discussed below.

FIGS. **35**A-**35**B illustrate reference Raman spectra of methylphenanthrene, one of homologue of phenanthrene, in a concentrations range from 0.01 ppm to 10 ppm. The reference Raman spectra show Raman spectral signatures about 540 $cm^{-1}$ and 1350 $cm^{-1}$. FIG. **35**C illustrates reference Raman spectra of 4-6 methyl dibenzothiophenes (MDBTs), one of homologue of dibenzothiophene (DBT), in concentrations ranging from 0.01 ppm to 10 ppm. The reference Raman spectra show Raman spectral signatures about 592 $cm^{-1}$. These spectral signatures can be used to analyze nano-surface-enhanced Raman spectra obtained from drilling samples obtained from different depths underground (from 2100 meter to 2458 meter deep), as shown in FIG. **34**, which identifies content dibenzothiophene's family member(s) in the drilling samples. The existence of dienzothiophene family member(s) in the drilling sample serves as an indicator for the probability of crude oil and gas underground. Other molecules that can provide Raman spectral signatures for detecting oil and gas content in drilling samples include aromatic molecules and multi-ring aromatic molecules such as thiophene, dibenzothiophene, methyl dibenzothiophene, 4,6 methyl dibenzothiophene, methylphenanthrene, and carbazole and their homologue compound molecules, respectively. Other molecules suitable for n-Hexane, Cyclohexane, Benzene, Toluene, Xylene (including m-Xylene, o-Xylene, and p-Xylene), Octane, Heptane, Noname, and other hydrocarbon compounds such as sulfur or nitrogen containing hydrocarbon compounds such as carbazole and its homologue compound molecules, and dibenzothiophene and its homologue compound molecules.

In some embodiments, since nano-surface enhanced Raman spectral analysis is highly sensitive, the presently disclosed method is capable of detecting substances that are partially evaporated in the drilling samples (during the drilling, or after the drilling sample is obtained but before the measurement). In other words, the presently disclosed method is especially advantageous for hydrocarbon molecules that have low boiling or vaporization temperatures, which are often rich in the content of crude oil or gas. For example, the substance associated with the Raman spectral signature(s) suitable for the present method can be a hydrocarbon compound that has a boiling temperature or a vaporization temperature below 100° C., which are difficult, as described above, for the conventional methods to detect due to loss of evaporation materials during drilling and material handling and transfer from drilling well to the lab.

The presently disclosed method of identifying molecules using nano-surface-enhanced Raman spectra has been compared to conventional testing method such as gas chromatography (GC). Close correlation was found between the presently disclosed method and GC testing techniques. However, the presently disclosed method only took 20 minutes in the field at the location of the drilling hole, whereas the conventional GC method took over 4 hours, or even over 15 hours, to complete.

Determining Mineral Compositions in Rock Samples to Predict Probability of Crude Oil or Gas Underground

In some embodiments, Raman spectral analysis can be used to determine mineral composition and distribution on rock samples extracted from underground in crude oil and gas exploration.

FIG. **36** illustrates an exemplified process for detecting mineral compositions in rock samples to determine probability of crude oil or gas underground. First, Raman spectral signatures of common minerals in rock samples are established (step **3610**). FIGS. **37**A-**37**E illustrate Raman spectra, respectively, associated with several common minerals: Quartz, Calcite, Plagioclase, Dolomite, and Hornblende. As shown, each of the Raman spectra includes one or more spectral signatures (Raman spectral peaks) at specific Raman shift in wavenumber.

Next, quantitative dependences of the spectral intensities at the Raman spectral signatures are established as a function of the concentration of the common minerals (step **3620**). FIGS. **38**A-**38**C show experimentally obtained Raman spectral intensities at the spectral signatures as a function of concentration for Quartz, Plagioclase, and Calcite, which are common in rock samples.

A sliced rack sample (FIG. **39**) is obtained by slicing a rock core sample obtained from underground. As shown in FIGS. **40**A and **40**B, sample dot arrays are respectively defined on the top and the bottom surfaces of the sliced rock sample (step **3630**).

Similar to steps **3040**-**3060** in FIG. **30** (except that no sample solution of nano particles is involved here), each sample dot on the surface of the sliced rock is illuminated by a laser beam (step **3640**). The light scattered by the surface of the sliced rock at each sample dot is collected (step **3650**). A Raman spectrum is obtained collected the scattered light from each sample dot on the surface of the sliced rock (step **3660**).

A main mineral ingredient is determined at each sample dot on the surface of the sliced rock sample (step **3670**) using the Raman spectral signatures at specific Raman shift wavenumbers to identify mineral type. Concentration of each main mineral type at each sample dot can be obtained using the Raman spectral intensity at the Raman spectral signature using the functional relationships as exemplified in FIGS. **38**A-**38**C. As shown in FIGS. **40**A and **40**B, a map of different types of mineral content (as well as each main mineral's concentration) is obtained across the sample dot array on the top and bottom surfaces of the sliced rock sample (step **3680**). The exemplified minerals include Quartz, Calcite, Plagioclase, Dolomite, Pyroxene, Chlorite, Kalifeldspar, Na-feldspar, Amphibole, MuscLaumontite, analcime ovite, Biotite, Ankerite, Siderite, Anhydrite, Gypsum, Thenardite, Barite, Pyrite, Glauberite, Laumontite, Analcime, Illite, Smectite, Kaolinite, Corundum, Ankerite, or Halite. Other minerals suitable for the presently disclosed method include Mica, Hornblende, and Granite.

FIG. **41** shows concentration mapping of plagioclase across an array of sampling dots on the top surface of the sliced rock sample in FIG. **39**. The mineral compositions is used to predict probability of crude oil or gas underground (step **3690**). Typically, a database of historic data is stored relating to correlations between mineral compositions and known oil/gas content. The historic data can be used to predict oil content based on the mineral compositions using Raman mapping method. As comparison result, targeted mineral sample concentration in a rock sample obtained by rock surface Raman mapping shows good correlation with the results of the X-ray analyses.

It should be noted that the disclosed Raman spectral analysis of mineral compositions in rock samples is not limited to sliced rock samples; it can also be applied to powder rock samples.

It should also be noted that the disclosed Raman spectral analysis of mineral compositions in rock samples has been found to correlate with conventional GC method very well. However, similar to the surface-enhanced Raman analysis method disclosed above, the disclosed Raman spectral analysis of mineral compositions in rock samples can be conducted much faster than conventional testing techniques: for example, a conventional X-ray measurement may take days to finish while the presently disclosed methods usually only take minutes. The presently disclosed method is thus more convenient (in field) and lower cost to implement.

Predict Probability of Crude Oil or Gas Underground by Analyzing Drilling Sample and Rock Samples

It should also be noted that the disclosed Raman spectral analysis of mineral compositions in rock samples (FIG. **36**) and the surface-enhanced Raman analysis of substances in drilling samples (FIG. **30**) can be combined. Both methods can be implemented in the field. Correlation of the results from the two disclosed methods can improve accuracy and confidence in determining the presence as well as concentrations of oil or gas underground.

The combined method for predicting presence of crude oil or gas underground can include one or more of the following steps: first, a drilling sample and a sliced rock sample are obtained from a same geological location. They can be obtained from a same drilling hole, or from different drilling holes. The drilling sample (typically in a fluid or mud form) is introduced into a sample solution containing nano particles. The sample solution comprising the drilling sample and the nano particles is illuminated by a first laser beam emitted by a probe (usually in the field). The probe collects light scattered by the drilling sample and the nano particles in the sample solution. A first Raman spectrum is obtained from the light scattered by the drilling sample and the nano particles in the sample solution. A spectral signature associated with a substance is identified around a predetermined Raman shift in the first Raman spectrum. The substance is known to be present in crude oil or gas. Crude oil or gas content is determined in the drilling sample based on the spectral signature of the substance in the first Raman spectrum. Similarly, the surface of the sliced rock sample is illuminated by a second laser beam. The second laser beam can be produced by the same probe. Light scattered by the surface of the sliced rock sample at each of the sample dots is collected. A second Raman spectrum is obtained from the light scattered from the surface of the sliced rock sample at each of sample dots. A mineral content is determined at each of the sample dots on the surface of the sliced rock sample based on the second Raman spectrum. A probability of crude oil or gas underground is predicted based on the mineral content and the crude oil or gas content in the drilling sample.

Monitoring Network System for Detecting Oil Content in Drilling Samples and Mineral Compositions in Rock Samples in the Field

In some embodiments, referring to FIGS. **26-27**, **30**, **36**, the processes shown in FIGS. **30** and **36** can be implemented by the monitoring network system **2600**. The presently disclosed mobile detector **2620** is deployed near the drilling holes where the drilling samples and rock samples are extracted from underground. The probe **2621** (i.e. probe **3150** in FIG. **31**) emits laser incident light to illuminate a sample solution (**3120** in FIG. **31**) comprising nano particles and the drilling sample, or the surface of a sliced rock sample (e.g. as shown in FIG. **39**). The probe **2621** also collects light scattered by the sample solution or the surface the sliced rock sample. Raman spectrum is obtained by the spectrometer **2740** in the mobile detector **2620**.

In some embodiments, one or more mobile detectors **2620** can be installed inside a drilling hole underground to provide real-time, in-field, and "in-depth" (literally and metaphorically) monitoring of the chemical content of the substance in the drilling hole. The mobile detectors **2620** can be connected the network using durable cables which can hold data and power lines, a wireless method. Different mobile detectors **2620** can be installed at different depths underground to enable real-time data at different drilling depths as exemplified by FIG. **34**. The steps of illuminating the sample and collecting light from the sample are conducted by a mobile detector **2620** in the drilling hole underground. Optionally, Raman spectra are also obtained in the drilling hole underground. The Raman spectral data is transmitted electronically from underground to the equipment and network above ground.

The spectral data can be analyzed in the mobile detector **2620**, or can be transmitted the central office **2610** for analyses. As described above, the analyses can involve identifying spectral signatures of certain substances that is rich in oil or gas, or identifying spectral signatures of certain minerals. The analyses can further include comparing to predetermined thresholds for the substances to predict oil or gas with confidence. The analyses can also include comparing to measured mineral compositions in the rock sample to a predetermined range to reliably predict oil or gas underground. The analyses algorithms, the thresholds, and the predetermined ranges can be stored locally in the mobile detector **2620**, or can be stored in the database **2670** and executed by the server **2640** in the central office **2610**.

One advantage of the presently disclosed methods is that by providing testing in the field, feedback and guidance can be provided almost real time to the drilling strategies in the field. For example, if a drilling hole or rock core show promising oil/gas content at different depths underground (e.g. by analyzing Raman spectral signatures at different depths of the drilling holes as shown in FIG. **34**), more drilling can be done at different depths or in the adjacent areas to explore detailed scope of the oil and gas deposits underground. If the in-field testing result is not promising at a location, the drilling team can quickly move on to the next location. Thus, the entire drilling exploration is made more efficient by the presently disclosed methods.

Another advantage of the presently disclosed methods is that the central office can instantaneously monitor testing results from multiple locations in the field, which allows the monitoring network system **2600** to have a global picture for potential oil and gas deposits in a large geological area.

In should understood that the foregoing description and examples, limited and narrow interpretation of descriptive language intended to better illustrate the invention is not to be construed as limiting in any way nor to limit the scope of the invention contemplated by the inventor. It will be clear that the invention may be practiced otherwise than as particularly described in the foregoing description and examples. Numerous modifications and variations of the present invention are possible in light of the above teachings and, therefore, are within the scope of the appended claims.

What is claimed is:

**1**. A method for detecting crude oil or gas in a drilling sample, comprising: extracting a drilling sample from a first drilling hole in a ground; introducing the~drilling sample into a sample solution containing nano particles; illuminating the sample solution comprising the drilling sample and the nano particles by a laser beam in the vicinity of the first drilling hole; collecting light scattered by the drilling sample and the nano particles in the sample solution; obtaining a Raman spectrum from the light scattered by the drilling sample and the nano particles in the sample solution; identifying, in the Raman spectrum, a spectral signature associated with a substance around a predetermined Raman shift; determining crude oil or gas content in the drilling sample based on the spectral signature of the substance in the Raman spectrum; and in response to the crude oil or gas content determined in the drilling, adjusting drilling depths or locations of one or more drilling holes in real time.

**2**. The method of claim **1**, wherein the drilling sample is collected in a first drilling hole underground, wherein the steps of illuminating the sample solution and collecting light are conducted by a detector in the drilling hole underground.

**3**. The method of claim **2**, wherein the substance comprises at least one of a multi-ring aromatic molecule, thiophene, dibenzothiophene, methyl dibenzothiophene, phenanthrene, methylphenanthrene, carbazole, or a homologue of aforementioned molecules, n-hexane, cyclohexane, benzene, toluene, or xylene, otctane, heptane, or nonane.

**4**. The method of claim **1**, wherein the substance comprises aromatic molecules.

**5**. The method of claim **1**, wherein the substance comprises nitrogen containing hydrocarbon compounds.

**6**. The method of claim **5**, wherein the nitrogen containing hydrocarbon compounds include carbazole or homologue compound molecules of carbazole.

**7**. The method of claim **1**, wherein the substance comprises sulfur containing hydrocarbon compounds.

**8**. The method of claim **7**, wherein the sulfur containing hydrocarbon compounds include dibenzothiophene or homologue compound molecules of dibenzothiophene.

**9**. The method of claim **1**, wherein the spectral signature includes at least one spectral peak around the predetermined Raman shift, the method further comprising:

determining a concentration of the substance in the drilling sample using the spectral signature.

**10**. The method of claim **1**, further comprising:

after the step of introducing, allowing molecules in the drilling sample to adsorb to the nano particles in the sample solution.

11. The method of claim 1, wherein the sample solution comprises multi-valence ions.

12. The method of claim 1, further comprising:
introducing an ionic material into the sample solution, wherein the sample solution has an ionic concentration in a range from about 10 μM to a saturation level.

13. The method of claim 1, wherein the nano particles comprise a magnetic or ferromagnetic material.

14. The method of claim 13, further comprising:
applying an electrical field, a magnetic field, or an electromagnetic field to the sample solution during the step of collecting.

15. The method of claim 1, wherein the nano particles comprise a material selected from a group consisting of a metal, a metal alloy, an oxide material, silicon, a polymeric material, carbon nano tubes, and a combination thereof.

16. The method of claim 1, wherein the nano particles have an average dimension in a range from about 1 nm to about 10 μm.

17. The method of claim 16, wherein the nano particles have an average dimension in a range from about 5 nm to about 500 nm.

18. The method of claim 1, wherein the nano particles have a size distribution characterized by an average dimension and a width, wherein the ratio of the width to the average dimension is in a range from about 0.01 to about 3.

19. A method for predicting presence of crude oil or gas in the underground, comprising:
defining an array of sample dots on a surface of a sliced rock sample obtained from underground;
illuminating each of the sample dots on the surface of the sliced rock sample by a laser beam;
collecting light scattered by the surface of the sliced rock sample at each of the sample dots;
obtaining a Raman spectrum from the surface of the sliced rock sample at each of sample dots;
determining a mineral content at each of the sample dots on the surface of the sliced rock sample based on the Raman spectrum;
obtaining a map of mineral content on the surface of the sliced rock sample; and
predicting a probability of crude oil or gas underground using the map of mineral content.

20. The method of claim 19, further comprising:
establishing Raman spectral signatures in a plurality of minerals, wherein the step of determining a mineral content includes identifying a Raman spectral signature associated with one of the plurality of minerals in the Raman spectrum.

21. The method of claim 20, further comprising:
for at least one of the plurality of minerals, establishing a quantitative dependence of spectral intensity at one of the Raman spectral signatures as a function of the concentration of the one of the plurality of minerals, wherein the step of determining a mineral content includes calculating a concentration of the one of the plurality of minerals based on the function and spectral intensities at the spectral signature.

22. The method of claim 19, wherein the sliced rock sample is extracted from a first drilling hole in the ground, and wherein the steps of illuminating and collecting light are conducted in the vicinity of the first drilling hole.

23. The method of claim 22, further comprising:
in response to the map of mineral content on the surface of the sliced rock sample, adjusting drilling depths or locations of one or more drilling holes in real time.

24. The method of claim 19, wherein the mineral content includes one or more of Quartz, Calcite, Plagioclase, Dolomite, Pyroxene, Chlorite, Kalifeldspar, Na-feldspar, Amphibole, MuscLaumontite and analcime ovite, Biotite, Ankerite, Siderite, Anhydrite, Gypsum, Thenardite, Barite, Pyrite, Glauberite, Laumontite, Analcime, Illite, Smectite, Kaolinite, Corundum, Ankerite, Halite, Mica, Hornblende, or Granite.

25. A method for predicting presence of crude oil or gas in the underground, comprising:
receiving a drilling sample and a sliced rock sample obtained from a same geological location;
introducing the drilling sample into a sample solution containing nano particles;
illuminating the sample solution comprising the drilling sample and the nano particles by a first laser beam;
collecting light scattered by the drilling sample and the nano particles in the sample solution;
obtaining a first Raman spectrum from the light scattered by the drilling sample and the nano particles in the sample solution;
identifying, in the first Raman spectrum, a spectral signature associated with a substance around a predetermined Raman shift;
determining crude oil or gas content in the drilling sample based on the spectral signature of the substance in the first Raman spectrum;
illuminating a surface of the sliced rock sample by a second laser beam;
collecting light scattered by the surface of the sliced rock sample at each of the sample dots;
obtaining a second Raman spectrum using the light scattered from the surface of the sliced rock sample at each of sample dots;
determining a mineral content at each of the sample dots on the surface of the sliced rock sample based on the second Raman spectrum; and
predicting a probability of crude oil or gas underground using the mineral content and the crude oil or gas content in the drilling sample.

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